THE REDUCTION POTENTIAL OF PENTAVALENT VANADIUM TO VANADYL ION IN HYDROCHLORIC ACID SOLUTIONS

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FLUORESCENZVERSUCHE AN ORGANISCHE DAEMPFE, BESONDERS AN ACETON

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STUDIES OF THE NATURE AND REACTIONS OF OXIDIZED SILVER COMPOUNDS, ESPECIALLY IN NITRIC ACID

Thesis by

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In Partial Fulfillment of
Requirements for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1935

Abstract

I

A series of measurements of the electromotive force of half-cells made up of solutions of V_2O_5 and $VOCl_2$ in excess HCl against calomel half cells in HCl of the same strength, for which there were negligible liquid junctions, is presented. The acid concentration was varied from 0.01012 to 2.146 M. The observed potentials were corrected for calomel cell and for other concentrations as per the following assumed reaction:

$$VO^{++} + 2\ H_2O \quad == \quad HVO_3 \quad + \quad 3\ H^+ \quad + \quad E^-.$$

Values of E_0 so obtained decreased with decreasing acid concentration. This decrease was correlated with complex formation ($V(OH)_4^+$, etc.) noted in increased solubility of freshly precipitated HVO_3 in HCl as measured. The potential in molal HCl is -1.0216 volts, corresponding to a free energy decrease of +23,572 cal. when 1/2 H_2 reduces a pentavalent atom of vanadium (irrespective of nature) in 1.00 M HCl. From the temperature coefficient of the cell, the heat content increase for the same reaction was found to be -29,350 cal.

II

Experiments carried out in the Physico-chemical Institute of the Technische Hochschule München in searching for a discrete fluorescence spectrum of acetone vapor are given. A detailed description of the apparatus for studying flowing gases at various pressures is included, as well as a study of benzene fluorescence which was used to standardize technique and test the sensitivity of the methods. Long illuminations of acetone vapor at various pressures with powerful Al sparks gave no fluorescence, although the line 1862 Å was absorbed. A mercury arc produced in short time three continua in the visible, two of which were already known, but no line spectrum. Conditions were found with Tesla excitation in which output of light was good but little CO was formed in decomposition. Nine hours exposure yielded only the continua mentioned. Preliminary work was done on methyl iodide.

III

The analytical chemistry of bivalent silver solutions is discussed, especially the exact $TlNO_3$ method and the rapid $Cr(NO_3)_3$ method. Conditions prevailing in anodic oxidation are outlined, as well as a convenient method for preparation of solution. The main work deals with the complicated kinetics of oxidation of water by argentic silver at 25° and at 0°. The rate of decomposition of the argentic silver solution may be represented at constant acid by the equation:

$$-\frac{d\,(Ag^{++})}{d\,t} = k_2\frac{(Ag^{++})^2}{(Ag^+)} + k_4\frac{(Ag^{++})^4}{(Ag^+)}\ .$$

where k_2 varies roughly inversely as the square of the hydro-

A b s t r a c t

gen ion concentration and is not greatly decreased by increasing ionic strength while k_4 falls off very rapidly with increasing acid and ionic strength. The mechanism seems to involve tervalent silver. From existent data the free energies of formation at 0° C. of the following are calculated: Ag^{++}, Ag_2O_3, AgO, Ag_2O, O_3, H_2O and Ag^+, and a number of equilibria involving them are predicted and discussed.

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[Reprint from the Journal of the American Chemical Society, 55, 1909 (1933).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 347]

The Reduction Potential of Vanadic Acid to Vanadyl Ion in Hydrochloric Acid Solutions

BY CHARLES D. CORYELL AND DON M. YOST

Introduction

Earlier investigations of cells involving pentavalent and tetravalent vanadium gave values of -0.92 volt[1] and -1.0 volt[2] for the molal reduction potential in sulfuric acid solutions. Abegg, Auerbach and Luther[3] base their figure of -1.20 volts on the first mentioned determination. Uncertain liquid junction potentials diminish the reliability of these determinations, and the undetermined part that the acid concentration plays in the cell reactions introduces uncertainty in the interpretation of the published values.

In this paper are presented the results of measurements on cells in which the potentials due to liquid junctions are practically eliminated. Hydrochloric acid solutions of the vanadium compounds were used rather than sulfuric acid solutions because it is in chloride solutions that a knowledge of the reduction potential is most often desired. This is, for example, the case in applications to qualitative analysis.[4]

(1) Rutter, *Z. anorg. Chem.*, **52**, 368 (1907).

(2) Foerster and Böttcher, *Z. physik. Chem.*, [A] **151**, 321 (1930).

(3) Abegg, Auerbach and Luther, "Messungen elektromotorische Kräfte galvanische Ketten," Halle A.S., Wilhelm Knapp, 1911, p. 199.

(4) See, for example, Noyes and Bray, "Qualitative Analysis of the Rare Elements," Macmillan Co., New York, 1927.

The cell whose electromotive force was determined is

$$\text{Pt, } \begin{matrix} VOCl_2\ (c'\text{ f.}) \\ HVO_3\ (c''\text{ f.}) \\ HCl\ (c_A\text{ f.}) \end{matrix}, HCl\ (c_A\text{ f.}), HgCl\ (s) + Hg\ (l) \qquad (1)$$

The concentrations of vanadic acid and vanadyl salt were kept low, and the hydrochloric acid was present at the same concentration in both half-cells in order to make the liquid junction potentials negligible.

Preparation of the Materials and Experimental Procedure

The stock solutions of vanadyl chloride were prepared by the method described by Yost and Claussen.[5] The total chloride present was determined gravimetrically by precipitating it as silver chloride, and the vanadyl salt was determined by titration with standard permanganate.

Vanadic acid solutions were prepared by dissolving vanadium pentoxide in hydrochloric acid of known strength. The pentoxide was made from recrystallized ammonium metavanadate by carefully heating the salt in a stream of oxygen. The small amount (1%) of vanadium dioxide present as impurity was determined and allowed for in calculating the final concentration of hydrochloric acid. The method developed by Ramsay[6] was employed for the analysis of the vanadic acid solutions.

The hydrochloric acid and mercury were carefully purified, and the calomel was prepared as described by Ellis.[7]

The densities of the solutions were determined so that the concentrations could be expressed in terms of formula weights per 1000 g. of water.

The Pyrex glass cell was a modification of the design developed in this Laboratory. The stopcocks connecting the half-cells were so surrounded by glass that no contact with the thermostat liquid was possible. The presence of three calomel half-cells and two vanadium half-cells, all interconnected, made possible various combinations and checks. Observations on the electromotive force of a cell were begun about an hour after the cell had been placed in the thermostat, and were then continued at suitable intervals for a period of about one week.

The measurements were made at 25.00 and at 33.90°. Accurately reproducible results and constancy were not attained in all cases, until a small amount of ferric chloride was added to the vanadium solutions. The quantity added was so small a fraction (0.05%) of the total vanadium concentration that it could not affect materially the concentration of the latter substance. With hydrochloric acid concentrations of 0.25 f. and lower no ferric chloride was added since constancy and reproducibility were attained without its use.

Results of the Electromotive Force Measurements at 25°

Table I contains representative results of the electromotive force measurements made at 25.00°. Each observed value E is the average for two cells, in each of which equilibrium had been reached and maintained for twenty-four hours. The electromotive forces of individual cells rarely varied by more than ±0.2 millivolt, except in those cases where the hydrochloric acid concentrations were 0.01012 f. and 2.146 f. All concentrations are given in formula weights per 1000 g. of water.

(5) Yost and Claussen, THIS JOURNAL, **53**, 3350 (1931).
(6) Ramsay, *ibid.*, **49**, 1138 (1927).
(7) Ellis, *ibid.*, **38**, 737 (1916).

TABLE I

RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS AT 25°

Expt.	Formal concentration HCl	Formal concentration $VOCl_2$	$\frac{(HVO_3)}{(VOCl_2)}$	Electromotive force E (obs.)	Electromotive force E″ (calcd. by Eq. 2)	Mean
1	2.146	0.01518	0.8090	−0.8217	−0.8272	
2		.02269	.2705	.7943	.8279	
						−0.8276
3	1.031	0.01992	1.6094	−0.7621	−0.7499	
4		.02974	0.8090	.7442	.7496	
5		.01487	.8090	.7448	.7503	
6		.01487	.8090	.7447	.7502	
7		.03954	.4054	.7276	.7508	
8		.01977	.4054	.7272	.7504	
9		.01977	.4054	.7267	.7499	
10		.04445	.2705	.7163	.7499	
						−0.7501
11	0.5106	0.00986	1.6094	−0.6985	−0.6863	
12		.01472	0.8090	.6808	.6863	
13		.01472	.8090	.6804	.6858	
14		.01472	.8090	.6805	.6859	
15		.00736	.8090	.6805	.6860	
16		.01957	.4054	.6633	.6865	
						−0.6861
17	0.2541	0.007317	0.8090	−0.6228	−0.6283	
18				.6229	.6283	
19				.6221	.6276	
20				.6222	.6277	
						−0.6280
21	0.1013	0.002917	0.8090	−0.5496	−0.5551	
22				.5485	.5540	
23				.5497	.5552	
24				.5485	.5539	
						−0.5546
25	0.05061	0.001458	0.8090	−0.4958	−0.5013	
26				.4957	.5012	
						−0.5013
27	0.01012	0.0002912	0.8090	−0.3703	−0.3758	
				.3702	.3757	
						−0.3758

In the last column of Table I are given values of the electromotive forces E″ calculated from the equation

$$E'' = E + 0.05915 \log \frac{(HVO_3)}{(VO^{++})} \qquad (2)$$

It will be noted that the values of E″ for different vanadium concentrations at fixed hydrochloric acid concentrations are constant within the limits of experimental error; this shows that the activity coefficients of the two vanadium compounds are constant, and both contain the same number of vanadium atom.

The mean values of E″ given in Table II represent the electromotive forces at 25° resulting from the following change in state

VO^{++}(c f. in c_A f. HCl) + $2H_2O$ (in c_A f HCl) + HgCl(s) =
HVO_3(c f. in c_A f. HCl) + $3H^+$ (in c_A f. HCl) + Cl^- (in c_A f. HCl) + Hg(l) (3)

The vanadium half-cell potential, E′, referred to the standard hydrogen electrode is obtained by adding to E″ the electromotive forces produced by the following two reactions

Cl^- (in c_A f. HCl) = Cl^- (act. 1 m.); $E = 0.05916 \log c_A \gamma_A$ (4)
Hg(l) + Cl^-(act. 1 m.) = HgCl(s) + E^-(1 m.); $E = E_{0\,(HgCl)}$ (5)

The values of the mean ion activity coefficient γ_A of the hydrochloric acid at its prevailing concentration c_A formal are given by Randall and Young,[8] and the molal electrode potential of the calomel electrode is −0.2689 volt.[9] Thus the values of E′ (equal to E″ − 0.2689 + 0.05915 log c_A γ_A) are indicative of the oxidizing power of vanadic acid in c_A formal hydrochloric acid, and such values are the ones to be used in practical applications of the results.

If it is assumed that the activity coefficient of the hydrogen ion is equal to the mean ion activity coefficient γ_A of hydrochloric acid, the electrode potentials $E_0 = E' + 0.05915 \log c_A^3 \gamma_A^3$ may be calculated, and are presented in the fifth column of Table II. In calculating the values for E_0 no correction has been made for the activity coefficients of vanadyl ion and vanadic acid, or for the changing activity of the water.

TABLE II

REDUCTION POTENTIALS OF VANADIC ACID TO VANADYL ION IN HYDROCHLORIC ACID OF VARIOUS CONCENTRATIONS AT 25°

Hydrochloric acid		Electromotive forces		
c_A formal	Act. coeff. γ_A	E″	E′	E_0
2.146	1.065	−0.8276	−1.0753	−1.0115
1.031	0.8147	.7501	1.0235	1.0369
0.5106	.7572	.6861	0.9794	1.0527
.2541	.7596	.6280	.9392	1.0659
.1012	.7954	.5546	.8882	1.0822
.05061	.8285	.5013	.8517	1.0962
.01012	.9037	.3758	.7653	1.1271

Discussion of the Reduction Potentials at 25°

Table II shows that the reduction potential E′ for the conversion of vanadic acid to vanadyl ion in 1.031 f. hydrochloric acid solution at 25° is −1.0235 volts. This is much greater than the potential (−1.3594 volts) for the reaction Cl^-(1 m.) = $\frac{1}{2}Cl_2$(1 atm.) + E^-, but only a little above the potential (−1.0659 volts) for Br^-(1 m.) = $\frac{1}{2}Br_2$(l) + E^-.

(8) Randall and Young, THIS JOURNAL, 50, 989 (1928).

(9) This value of −0.2689 volt is the molal electrode potential of the calomel cell for the case in which oxygen is not excluded. A number of investigators have found this cell to be reproducible and constant (Ref. 8) and because of its practical convenience it appears to be a desirable experimental standard. The activity coefficients of Randall and Young have been used to obtain this value, −0.2689 volt, which should replace the older one, −0.2700 volt, given by Lewis and Randall ("Thermodynamics," McGraw-Hill Book Co., N. Y., 1923). Evidently the value for oxygen-free cells, −0.2676 volt, determined by Randall and Young cannot be applied to the results with cells in which air is present.

In fact, in 2.145 f. hydrochloric acid the value of −1.0753 volts is somewhat below this latter potential. In as dilute acid as 0.0101 f. the potential (−0.7653 volt) is still considerably less than that of I^-(1 m.) = $^1/_2I_2$(s) + E^- (−0.5357 volt), however.

The values of the standard electromotive forces E_0 given in Table II show, even though the hydrogen-ion activity has been already corrected to unit activity, that the reduction potential of vanadic acid to vanadyl ion varies greatly with the acid concentration. Any decrease in the ion activity coefficient of vanadyl ion with increasing acid concentration would increase this variation still more. The effect of acid seems then to arise principally from the effect of the hydrochloric acid on the vanadic acid. The following considerations and experiments confirm this view.

It was found that the solubility of moist vanadium pentoxide in hydrochloric acid increases rapidly with the acid concentration, and this results in a corresponding decrease in the activity coefficient of the vanadic acid.[10] To correlate this fact with the results of the potential measurements, the activity coefficients of vanadyl ion were assumed equal to those of barium ion[11] at the same ionic strength, and the activity coefficients of the vanadic acid were then calculated from the values of E_0. These coefficients were taken arbitrarily as unity in 0.101 m. hydrochloric acid. The results described are presented in Table III.

TABLE III

THE SOLUBILITY AND ACITIVITY COEFFICIENTS OF VANADIC ACID IN HYDROCHLORIC ACID

Formality of HCl	Act. coeff. HCl, $\gamma_{\pm}$	Act. coeff. VO^{++}(Ba^{++})	Solubility vanadic acid as HVO_3, f.	Activity coefficients of vanadic acid from e. m. f.'s	Activity coefficients of vanadic acid from solubilities
0.018	0.88	0.59	(0.0049)	5.0	(2.2)
.101	.80	.34	.0097	1.0	1.0
.254	.76	.23	.052	0.36	0.19
.503	.76	.16	.182	.15	.053
1.03	.81	.11	.220	.056	.044

As will be seen in the table the activity coefficients derived from solubility measurements are in as good agreement as could be expected with those calculated from electromotive force measurements. The rough agreement also furnished justification for the cell reaction assumed in Equation (3). It seems likely that the effect of the hydrochloric acid arises from the formation of complex ions or, as Professor Pauling has suggested, the ion $V(OH)_4^+$.[12]

(10) As a result of colloid formation the solubility of the pentoxide in 0.018 m. hydrochloric acid is too high and the corresponding activity coefficient is too low. In the table the values are placed in parentheses.

(11) The values were calculated from the data given by Scatchard and Tefft, THIS JOURNAL, 52, 2270 (1930).

(12) Later experiments have shown that the solubility of vanadium pentoxide in perchloric acid varies with acid concentration in the same way as found when hydrochloric acid was used. This is good evidence for the existence of an ion of the type $V(OH)_4^+$.

Due to lack of more precise information it is not possible at this time to evaluate the conventional standard reduction potential of vanadic acid to vanadyl ion. The values of E′ in Table II represent the potentials which are to be used in any applications under the conditions indicated. The value of E′ at the rounded hydrochloric concentration of 1.0 molal is −1.0216 volts, which corresponds to a free energy decrease of −23,572 cal.

The Temperature Coefficient of Electromotive Force and the Change in Heat Content Accompanying this Reaction

In order to determine the temperature coefficient of the electromotive forces, a number of cells were measured at 33.90° as well as at 25.00°. In Table IV are presented the results of these measurements. The values are given to more significant figures in this case, since individual cells showed variations that were smaller than the variations between different cells.

TABLE IV

RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS AT TWO TEMPERATURES

Cell	Formality of HCl	Temp., °C.	E. m. f. in volts E (obs.)	E″ (calcd.)	$\Delta E''$ volts	$10^5 \frac{\Delta E''}{\Delta T}$
3	1.031 m.	25.00	−0.76218	−0.74995	0.00544	61.2
		33.90	.75711	.74451		
5		25.00	.74481	.75027		
		33.90	.73926	.74487	.00540	60.8
6		25.00	.74471	.75017		
		33.90	.73911	.74472	.00545	61.3
7		25.00	.72766	.75086		
		33.90	.72159	.74547	.00539	60.6
8		25.00	.72715	.75035		
		33.90	.72114	.74502	.00533	60.0
9		25.00	.72679	.74999		
		33.90	.72060	.74448	.00551	62.0
					Mean	+61.0
13	0.5106	25.00	.68033	.68579		
		33.90	.67333	.67894	.00685	77.0
14		25.00	.68048	.68594		
		33.90	.67335	.67896	.00698	78.6
					Mean	+77.8

By applying the Gibbs–Helmholtz equation to the values of the temperature coefficient given in Table IV, after correcting for the corresponding coefficient of the calomel electrode in the same range,[7] the change in heat content accompanying the following reaction was calculated.

$$VO^{++} \text{ (in } c_A \text{ f. HCl)} + 2H_2O(l) = HVO_3 \text{ (in } c_A \text{ f. HCl)} + 3H^+ (c_A \text{ f.}) + \tfrac{1}{2}H_2(1 \text{ atm.})$$

when $c_A = 1.0$, $\Delta H = 29{,}350$ cal. and when $c_A = 0.5$, $\Delta H = 29{,}220$ cal.

At present there are no heat data with which these results may be compared.

Summary

Measurements have been made on the following cell at several acid concentrations and varying concentrations of vanadic acid and vanadyl chloride.

$$\begin{array}{l} \quad VOCl_2\ (c'\text{ f. in } c_A\text{ f. HCl}) \\ Pt,\ HVO_3\ (c''\text{ f. in } c_A\text{ f. HCl}),\ HCl\ (c_A\text{ f.}),\ HgCl(s),\ Hg(l) \\ \quad HCl\ (c_A\text{ f.}) \end{array}$$

The electromotive force of the cell varies greatly with the acid concentration, and normally with the concentration of vanadic acid and vanadyl ion. An explanation for the effect of the acid is offered.

The reduction potential E' at 25° with reference to the molal hydrogen potential as zero was found to be −1.0216 volts in molal hydrochloric acid, slightly greater than the bromine potential (−1.0659 volts) and considerably more positive than the chlorine potential (−1.3594 volts). The corresponding potentials at other acid concentrations are presented in Table II.

From the temperature coefficient of electromotive force the heat content increase accompanying the reduction by hydrogen of one mole of vanadic acid in hydrochloric acid solution to vanadyl ion and water was found to be −29,350 cal.

PASADENA, CALIFORNIA

RECEIVED NOVEMBER 28, 1932
PUBLISHED MAY 6, 1933

FLUORESCENZVERSUCHE AN ORGANISCHE DAEMPFE,

BESONDERS AN ACETON

FLUORESCENZVERSUCHE AN ORGANISCHEN DAMPFEN, BESONDERS ACETON

Die vorliegende Arbeit wurde am Physikalisch-chemischen Institut der Technischen Hochschule München unter Leitung von Herrn Professor Doktor Günter Scheibe ausgeführt.

Einleitung

Die Wirkungen zwischen Licht und Materie bilden eines der fruchtbarsten Forschungsinstrumente, das uns in den Atom- und Molekülbau einführen kann. Absorptionspektren werden für diesen Zweck sogar weit untersucht, aber deren logische Ergänzungen, die Fluorescenzspektren, sind ja viel weniger bekannt.

In der Absorption absorbiert ein Molekül eine bestimmte Frequenz von Licht und wird zu einem höheren Niveau erregt (oder absorbiert das Molekül kontinuerlich und auseinanderfliegt, weil das höhere Niveau einem unstabilen Zustand entspricht). Im Fluorescenzfall werden die Moleküle durch Lichtabsorption, Hochfrequenzerregung oder irgendeine andere Erregungsmethode erregt, und wird das abgegebene Licht beobachtet, das die Moleküle ausstrahlen bei Übergängen in verschiedene energieärmere Niveaus. Bei der Lichterregung ist das Fluorescenzspektrum eindeutiger, weil in diesem Fall gewöhnlich nur eine kleine Zahl von Termen angeregt werden, obwohl bei höherem Druck, Energie in allen beliebigen Termen

durch Stösse zweiter Art geteilt werden kann.

In der bekannten Fluorescenz von Benzol ist diese Behauptung als Tatsache bewiesen. Von zirka 1 mm. Druck auf ist die Fluorescenz vollkommen von der Erregungsart unabhängig -- obwohl diese Tesla Entladung, Quecksilber Bogen, Eisen oder Aluminium Funke sein kann. (Literatur Referenzen 3, 8, 9, 10) Dies wurde experimentell in den Vorversuchen dieser Untersuchung bewiesen. Anderseits, bei verschiedenen Lichterregungen unterhalb ungefähr des Drucks von 1 mm. ist das Spektrum von der Lichtart abhängig. (Lit. 8.)

Der mit Fluorescenz gebundene experimentelle Nachteil ist die geringe Lichtintensität, die man mit gewöhnlichen Lichtquellen bekommt. Jedoch mit möglichst starken Funken oder Bogen, sorgfältiger Abblendung von falschem und gestreutem Licht, und einem lichtstarken Spektrographen, lassen die Versuche sich noch mit Dampf bei niedrigem Druck ausführen. Gerade im Dampfzustand sind die Zwischenmolekülarwirkungen am geringsten und die Resultate am wertvollsten. Sogar in flüssigem Zustand oder in Lösung ist die Struktur meistens vollkommen verwaschen. Mit Hochfrequenz oder Teslaerregung besteht die Luminiescenz öfters aus dem höchst komplizierten vollkommenen Spektrum, und die begleitende starke Zersetzung beschlägt rasch die Fenster, was weitere Beobachtung hindert.

Von den bekannten Absorptionsbereichen (Lit. 11, 12, 14, 15, 16, 20, 22) ist es möglich, erwartete Fluorescenzgebiete auszurechnen. Zum Beispiel, hat Aceton bekanntlich die folgenden Absorptionen (siehe Referenzen oben): Diskretes Spek-

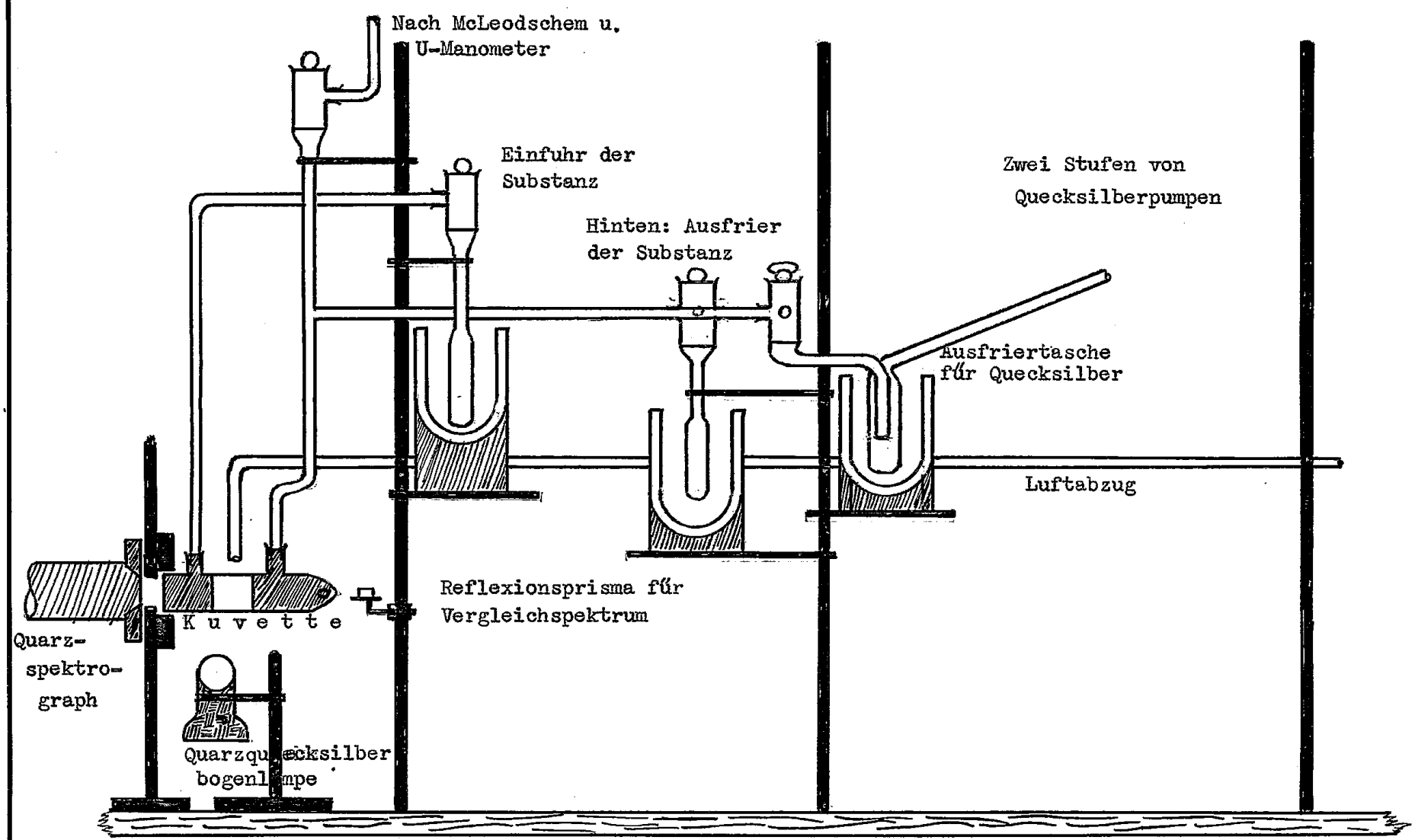
trum von 51430 cm^{-1} hinauf (1944 AE hinab); Kontinuum mit Maximum bei ca. 36500 cm^{-1} (2740 AE); Linienspektrum in der Nähe von 29000 cm^{-1} (3500 AE); und Bandspektrum im Ultrarot, 14000 - 9000 cm^{-1} (7200-1100 AE). Man soll eigentlich erwarten, zum Beispiel, von einer Erregung zum erst genannten Spektrumniveau, ein Kontinuum im Rot und Sichtbaren bei Übergang in den unstabilen Zustand, ein diskretes Spektrum im Violett und näherem Ultraviolett, weiterhin, eins im weiteren Ultraviolett (2300-2500 AE) vom Übergang in die Ultrarotterme, und ein Spektrum energetisch entsprechend ungefähr der ursprünglichenAbsorption vom Zurückfall zum Grundzustand. Norrish, Crone, und Saltmarsh (22) berichten kontinuerliche Fluorescenzübergänge die von Hg Linie 3342 erregt worden seien. Die von ihnen erst (20) erwähnte diskrete Fluorescenz fiel aus.

Diese hier vorliegende Arbeit besteht zum Teil von Versuchen, das von Aluminiumlinie 1862 AE vermutlich verursachte Spektrum zu erregen. Bis jetzt ist es niemand gelungen, diskrete Fluorescenz von Aceton zu erzeugen.

Ausführliche Beschreibung der Apparate

Der benutzte Q u a r z s p e k t r o g r a p h war von Zeiss geliefert, und hatte eine Öffnungsverhältnis 1 : 5. Die Brennkurve war stark gebogen, so dass ein Film verwendet werden muss. Die maximale Ablenkung wurde von Herrn Dörfling auf 2800 AE eingestellt, und hat eigentlich wenn wünschenswert auf eine kürzere Wellenlämge wiederhergestellt werden können.

S K I Z Z E 1



Gesamte Einrichtung

Falsches Licht wurde so weit wie möglich beseitigt, obwohl etwas unvermeidliche Linsenfluorescenz von weitem Ultraviolett vorkam. Die spektrographische Einrichtung wurde für diese Untersuchung möglichst günstig umgestellt, um maximale Empfindlichkeit zu erreichen.

Die Hochvakuum A p p a r a t u r ist in Figur 1 skizziert. Eine Vorratsflasche wird mit normalem Schliff einem Hahn angeschlossen, und hier wird durch Temperaturkontrolle mittels mit flüssiger Luft gekühltem Alkohol die untersuchte Substanz bei seinem beliebig erwünschten Dampfdruck erhalten. Die flüssige Luft wird durch eine Kupferschlange aus einer Dewarsche Spritzflasche geblasen, und die Temperatur mit der Hilfe eines Thermoelementes abgelesen. Diese Methode hat sich gut bewährt, aber konstanter Druck konnte noch besser bei dem Gefrierpunkt einer Flüssigkeit oder bei einem Eutektikumspunkt hergestellt werden.

Das Gas wurde gewöhnlich fliessend untersucht, um Zersetzungstörungen in der Kuvette oder Spektra von photochemisch erzeugten Zersetzungsprodukten zu vermeiden. Nach Ausgang von der Quarz Kuvette könnte das Gas in eine ähnliche Flasche ausgefroren werden. Ein besseres Verfahren für kleinere Drücke war, das Gas und irgendmögliche Zersetzungsprodukte, kondensierbar oder nicht kondensierbar, mit den Hochvakuumpumpen von der Apparatur auszupumpen.

Die Hähne und Schliffe sind mit Ramsay Hochvakuumfett gefettet. Die Kuvette wird mit Picein über der Quarz-Glas

Schliffverbindung gekittet. Hochvakuum (10^{-5} mm.) liess sich ziemlich leicht herstellen, und adsorbierte organische Substanzen nach einer Untersuchung liessen sich verhältnismässig leicht herausziehen. Druckzuhahme mit der Zeit war nicht sehr störend; zum Beispiel, nach 4 stündigem festem Auspumpen, stieg der Druck in der Abwesenheit von flüssiger Luft bloss 0,0003 mm. pro Stunde.

Der McLeodsche M a n o m e t e r mass Drücke von 10mm. bis 10^{-5} mm. Volumverhältnisse betrugen:

Tabelle 1. Eichung des McLeodschen Manometers.

Mark	v x 10^3			V		
1	7644	9	cm^3	122,99	0,1	cm^3
2	1762	9		128,87	0,1	
3	236,6	0,6		130,39	0,1	
4	41,9	0,3		130,49	0,1	
5	6,69	0,23		130,62	0,1	
6	1,43	0,16		130,63	0,1	

Druck $p = \frac{v}{V} \times h$ h = beobachtete Höhe des Fadens im Steigrohr wenn Faden im Druckrohr bei dem Mark ist.

Der Manometer wurde sehr sorgfältig gemacht und geeicht, aber der Kapillare Durchmesser (Druckrohrvolum 9,74 $mm^3/cm.$, Steigrohr 9,80 $mm^3/cm.$, d. h. ca. 1,1 mm. Durchmesser) war anscheinend zu eng ausgewählt. Man kann nicht wegen des Laufwiderstandes und des Springens vom Quecksilber dieselbe Höhe wiederherstellen mit einer Genauigkeit, im Fall der Marken 3 bis 6, die der Volumgenauigkeit entspricht.

Die Manometereinrichtung konnte von der übrigen Apparatur mittels eines Hahnes abgeschlossen werden. Folgende Tabelle schliesst einige Erfahrungen in der Herstellung von bestimmten Drücken. Höhere Drücke wurden am leichtesten mit stehendem Gas eingestellt, das so oft wie nötig gewechselt werden konnte; sie konnten auch durch die Auswahl von entsprechenden höheren Einstell- und Ausfrierdampfdrücken erreicht werden.

Tabelle 2. Druckerfahrung

Vorratsflaschedruck	Ausfrierflaschedruck	Gemessener Druck	Geschätzter Kuvettendruck	
24,4 mm.	3,9 mm.	5,8 mm	7 mm.	) Hauptdruckfall im 1en
3,9 mm.	24,4 mm.	8,2 mm.	7 mm.	) Hahn.
ca. 20 mm.	Auspumpen	6 mm.	7 mm.	(Viele Substanz ging verloren
6 mm.	Auspumpen	1,9 mm.	2 mm.	) Sehr bequem zu halten
0,6 mm.	Auspumpen	0,4 mm.	0,4 mm.	)

Die K u v e t t e wurde aus auf Durchlässigkeit für Aluminiumlinie 1862 AE ausgewählten, geschmolzenem Quarzrohr hergestellt, mit einem planem vorderem Fenster, und sie hatte ein auf dem anderen Ende ausgezogenes Horn. Innerer Durchmesser betrug 20 mm. Die Anschlüsse mit Quarz-Glas Schliffübergängen waren zu eng ausgewählt; der Schliff hatte nur 3 mm. inneren Durchmesser. Weiterhin, ist es ungünstig, Quarz als Mantelschliff zu haben, wegen der kleineren Wärmeexpansion; deswegen sollte etwas Kitt zwischen die Fläche eindringen. Diese Kuvette war damals so eingerichtet, dass die

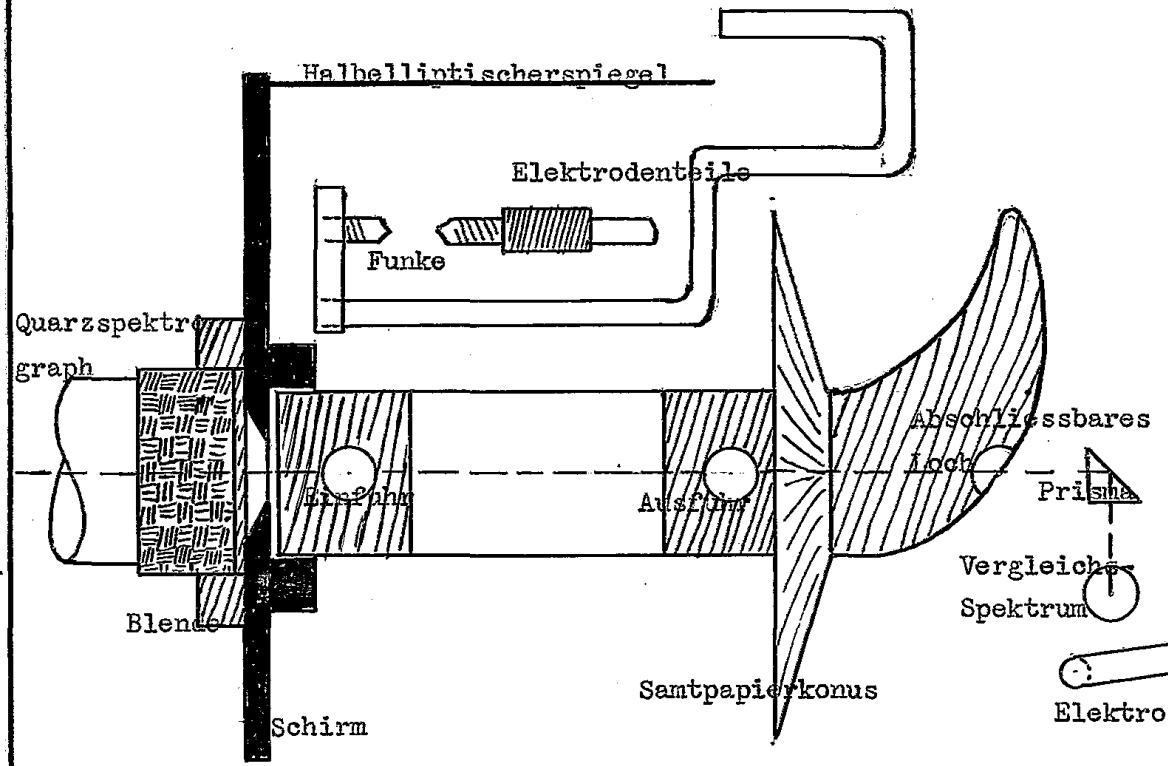
Anschlussrohre von oben angebracht waren. Diese Methode war günstiger für Flüssigkeiten; Drähte verbanden für Sicherheit die Kuvette mit Apparatrahmen. Die Kuvette war ungefähr 3 mm. zu niedrig eingebaut für die günstigste Beziehung zum Spektrographenspalt, obwohl dies nicht sehr störend wirkte.

Bei der Lichterregung von Benzol und Aceton war kein Niederschlag in der Kuvette bemerkbar. Jedoch bei Hochfrequenz- (Tesla-)entladung schlug sich öfters gelbes oder braunes Harz vor. Dieses liess sich am leichtesten bei mehrmaligen Ausspülen mit warmer Chromschwefelsäurelösung entfernen, oder eventuell bei Erwärmung der betreffenden Stelle durch eine kleine Flamme mit Hilfe dieser Säure.

Als L i c h t q u e l l e dienten Funken von verschiedenen Metallen oder eine Quecksilberbogenlampe. Im ersten Fall, wurden 6 mm. Stäbe des Metalls mit Gewinden vorgesehen, die in Kupfer-Aluminium-Elektrodenteilen eingeschraubt werden konnten. (Cf. Skizze 2). Der Funkenabstand war 7 oder 8 mm., und der Funke hatte seine Achse parallel der Kuvette ungefähr 23 mm. von deren Wand. Eine hoch-kondensierte Entladung von ungefähr 15000 Volt war durchgesandt. Ein Luftzug von einer Wasserstrahlpumpe zog einen grösseren Teil der schlechten staubigen Luft weg.

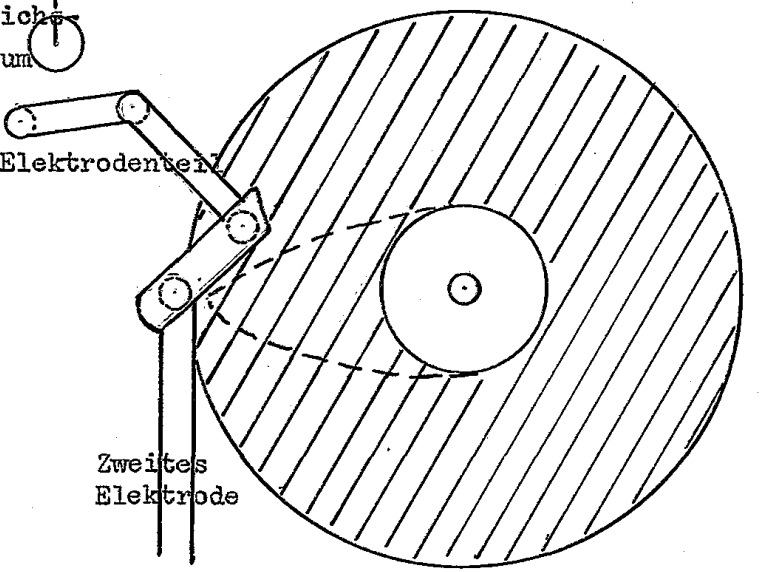
Rings um den Funken wurde ein elliptischer Spiegel eingebaut, mit Funken auf einer Fokalachse und Kuvetteachse auf der anderen, um Lichtverluste zu vermeiden. Später wurde nur eine Hälfte davon benützt, so dass man den Spiegel weg-

SKIZZE 2



Oberriss

Endriss
[ohne schirm]



nehmen konnte, um Kuvette und Spiegel von Elektroden-oxydstaub während einer Belichtung putzen zu können, ohne den Spektrographen berühren zu müssen. Für die kürzesten Wellenlängen hat ein Spiegel wenig Zweck, weil das Reflexionsvermögen von allen Metallen sehr klein ist. Die Kittestellen der Kuvette mussten gegen die Wärme geschützt werden, und gewöhnlich wurde ein Föhn zwecks Kühlung der Kuvette verwendet.

Ein wagerechter Quarzquecksilberbogen liess sich leicht unter die Kuvette und quer dazu einführen. Hier war Föhnkuhlung unbedingt notwendig. Die erreichte Intensität von 2500 AE aufwärts war mit der Lampe viel stärker als bei Funkenerregung.

Sehr interessant waren die mit H o c h f r e q u e n z - e r r e g u n g mit Hilfe von Herrn Daser gemachten Versuche. Zuerst war seine Vakuumrohr Hochfrequenzentladung mit besonder kontrollierbar, Frequenz und Spannung verwendet. Zwei Blech Aluminium dienten als Elektroden, und deren Entfernung die Eigenschaften des Leuchtens kontrolliert. Als bestes war ein gleichmässiges kühles Leuchten gehalten, das die minimale Spannung zum Sehen hatte. Man fand später, dass ringförmige Blechelektroden vorwärts an der Kuvette und beim Horn die am wenigsten störende Zersetzung (stark lokalisiert) verursachten, und der Niederschlag weit von Einstrahl- oder Spektrographenfenster ausfiel.

Es war auch gefunden, dass ebensogute Teslaerregung wurde von der kleinen Laboratoriumshochfrequenzapparatur.

geliefert. Diese hatte Probeelektrode, die in Verbindung mit den Ringen gebracht werden konnten. Die Spannung war durch Primärwiderstand leicht zu ändern.

Für diese Versuche war die A b b l e n d u n g sehr wichtig, um falsches Licht möglichst von dem Spektrographen abzuhalten. Das Horn an der Rückwand war mit schwarzem Lack so dick gestrichen, dass das von Aussen auftretende sowohl als das von Innen reflektierte Licht absorbiert wurde, und auch die beiden Ansatzrohre. Die vordersten 3 cm. der Kuvettenwände waren gleichfalls schwarz, um das Fenster vom direkten Funkenlicht zu schützen. Von Zentimeter 7 ab waren die Wände wieder geschwärzt, so dass das beträchtliche Streulicht und die leicht sichtbare Quarzfluorescenz davon nicht in den Spektrographen kommen konnten. Die Wandschwärzung war so bemessen, dass selbst wenn der Spektrograph einen Winkel von 2^{0} mit der Kuvettenachse bildete, bekam er kein direktes Streulicht. Ein Konus von Samtpapier hinter dem Ausfuhrrohr schloss Zimmerlicht von der Apparatur aus.

Zwischen der Kuvette und dem Spektrographen stand eine Blende, die alles Licht von dem Funken abschirmte, und nur eine Öffnung 5 x10 mm. für das Fluorescenzlicht vorsah. Alle Lichtquellen mussten so eingestellt werden, dass das einstrahlende Licht in der dem Spektrographenspalt entgegensetzten Richtung einstrahlte, so dass das mehrmalige in der Kuvette umreflektierte Licht nicht in den Spektrographen strömte.

Die V e r g l e i c h s p e k t r e n wurden als Funken oder Bogen neben der Kuvette erzeugt, und mit einem Quarzprisma entlang der optischen Achse der Kuvette reflektiert, durch eine axiale Öffnung in deren Horn durchgesandt. Diese Öffnung konnte, wenn nicht in Gebrauch, mit einem Samtpapierverschluss verschlossen werden. Die Einrichtung diente auch als Kontrolle in der Einstellung des Spektrographen auf der Kuvettenachse, wodurch man den Spalt sehr breit machte und feststellte, ob das durch den Spektrographen vom Spalt begrenzte Licht durch die Mitte des Systems kam. Die Lage des Spektrographen war mit fest geschraubten V-Klötzen vor den drei Füssen bestimmt.

Experimentelles

B e n z o l wurde zuerst untersucht, um die Leistung der Apparatur zu prüfen. Kahlbaums reinstes Benzol wurde viermal umkristallisiert, und hatte den konstanten beobachteten Gefrierpunkt 5,47°. Die erste Belichtung war mit dem Quecksilberbogen an fliessendes Gas bei ungefähr 15 mm. Druck gemacht und dauerte 3 Stunden. Sie lieferte eine schöne Fluorescenz mit 5 Bandgruppen. Eine so kurze Belichtungzeit wie 6 Minuten lieferte die charakterische Fluorescenz mit 4 Bandgruppe bei 8 mm. Druck.

Die Prüfung der Apparatur mit Funkenlicht geschah mit Aluminiumfunken 3 Stunden an Benzoldampf bei 10 mm., der eine schwache aber klare Fluorescenz lieferte, und mit einem

Eisenfunken an Benzoldampf bei 8 mm., der in bloss 1 Stunde eine gute Fluorescenz mit wenigem Streulicht erzeugte.

Weiterhin wurde ein Vergleich zwischen der von Eisen und Quecksilber erregten Fluorescenz gemacht, der zeigte, wie sie sich unterscheiden. (Literatur 3 durch 10 schliesst Benzolfluorescenz ein).

Mit Teslaerregung an Benzol bei 15 mm. Druck fand viele Zersetzung statt, und die helle Luminescenz lieferte bloss ein Kontinuum, das allerdings sehr breit war. Mit niedrigerem Druck und niedrigerer Spannung, so dass keine Luminescenz sichtbar war, trat in einer Stunde gar kein Spektrum hervor. Mit ungefähr 2 mm. Druck des fliessenden Gases und der ersten Spannung, die die sichtbare Luminescenz erregte, bekam man in 20 Minuten ein kräftiges "Hochdruckspektrum" mit 7 klaren Bandfolgen. Jedoch fand etwas Zersetzung in der Kuvette statt. Solche Zersetzung war immer störend; danach muss die Kuvette abgebaut und sorgfältig geputzt werden.

Diese Versuche und andere zeigten klar, dass man verhältnismässig schwache Fluorescenz beobachten kann, die entweder mit Quecksilber Bogen, verschiedenen Metallfunken, oder Hochfrequenzfeldern erregt werden. Falsches Licht rührte hauptsächlich von Kuvettenfluorescenz im Blau her, und stört nicht beträchtlich die Beobachtung. Die Versuchsmethode wurden gleichzeitig standardisiert.

Eine Besprechung über die möglichen Fluorescenzgebiete A c e t o n s findet sich in der allgemeinen Einleitung zu diesem Bericht. Es wurde in erster Linie versucht, die von den Aluminiumlinien 1862,5 / 62,9 AE verursachte Fluorescenz zu beobachten. Diese Linien treffen fast genau an der breiten Acetonabsorptionlinie B_3, 1861,8 AE, an, deren k gleich 960 sein soll (14), die nach Scheibe dem dritten Schwingungsquant des ersten Elektronensprungs zugeordnet ist.

Es wurde willkürlich angenommen, dass eine günstige Fluorescenz, die sich durch die ganze Kuvette verbreitet, erzeugt werden würde, wenn ungefähr 3/4 des erregenden Lichtes in der Kuvette absorbiert wäre; d. h. dass die Hälfte des Lichtes in dem ersten Zentimeter absorbiert sein soll, und danach, soll für die Mitte dieser Linie der Druck 0,25 mm. betragen. Reinstes Aceton wurde verwendet, das mittels der Bisulfitverbindung von Herrn Grieneisen gereinigt wurde.

Obwohl das Licht anscheinend stark absorbiert wird, wie quer der Kuvette aufgenommene Probeaufnahme zeigten, konnte überhaupt keine Spur von Fluorescenz bei ungefähr 0,5 mm. in 6 Stunden mit breitem Spalt (0,06 mm.) festgestellt werden. Weitere Versuche mit 3 Stunden Belichtungzeit sind vorhanden für ungefähr 0,2 mm., für 4 mm., und auch für 40 mm., alle gleichfalls ohne Erfolg.

Einige Versuche wurden mit anderen Erregungsarten durchgeführt. Der Quecksilberbogen bei 40 mm. Druck und bei 170

mm. Druck lieferte in einer halben Stunde eine Fluorescenz, die aus zwei Banden im Sichtbaren, sehr diffus aber stark, von 5000-5220 AE und von 5420-5650 AE entstand, und es könnte auch sein, dass da ein Band im Bereich 3500-4700 AE entstand, die von der Kuvettenfluorescenz bedeckt sein konnte. (Wegen des höhen Druckes erwartet man auch mehr Streuung von den Molekülen). Damon und Daniels (18) haben Banden 4100-4820 AE und 4990-5210 AE beobachtet. Nach dieser Arbeit veröffentlichten Norrish, Crone, und Saltmarsh Angabe über Kontinua 5034-5244 AE, 5458-5699 AE, und 5917-6303 AE, unter denen das erste und zweite mit meinen gut stimmen; das dritte konnte mein Film nicht aufnehmen. Kontrolle mit reinem Kohlenoxyd bei 40 mm. und bei 2 mm. zeigten keine Quecksilbererregte Fluorescenz von diesem bekannten Acetonzersetzungsprodukt.

Hochfrequenzversuche mit Aceton lieferten bei Drücken unter 2 mm. des fliessenden Gases immer Fluorescenz hauptsächlich von dem durch Acetonzersetzung erzeugten Kohlenoxyd. Bei nicht zu grossen Spannungen, und mit fliessendem Gas bei 2 mm., konnte man ein schönes kornblumenblaues Licht erhalten, und in einer neunstündigen Belichtungszeit erschienen die folgende Kontinua: ein starkes von 3340 bis 4770 AE, ein sehr schwaches von 5100-5200, und ein mässig starkes von 5460-5620. (Die letzten stimmen mit den von Quecksilberlicht überein). Ausserdem waren nur drei Kohlenoxydlinien zu sehen. Das Minimum der Empfindlichkeit des benützten Films liegte

zwischen 4900 und 5100 AE (grüne Lücke).

Acetonlösungen in destilliertem Wasser in den Konzentrationen, die den im Gas bei 0,3 und 3 mm. Molekularkonzentrationen entsprachen, wurden mit Aluminiumfunken 3 Stunden ohne Abwechselung der Lösung belichtet. Keine Fluorescenz wurde beobachtet. Bemerkenswert ist die Tatsache, dass sehr wenig Streu- und Quarzfluorescenzlicht vorhanden war.

Trotz sorgfältiger Versuche, gelang es nicht, ein diskretes Fluorescenzspektrum von Aceton zu bekommen. Es könnte sein, dass die vermutlich tätige Absorptionslinie B_3 Prädissoziation zeigt, und danach, wäre eine Fluorescenz nicht zu beobachten. Das ganze Spektrum ist wenig bekannt; eine erreichte Fluorescenz hätte vielleicht der Aufklärung viel geholfen. Es besteht die Möglichkeit, andere Absorptionslinie auszusuchen, unter denen, die bei 1900,4 AE, die vielleicht Sn Linie 1901,0 absorbiert. Es wäre auch wünschenswert B_3 noch mit Co Linie 1861,5 AE zu belichten.

In der Teslaluminescenz von Aceton entstand Kohlenoxyd als Zersetzungsprodukt, und gleichzeitig erschien sein bandreiches Spektrum auf dem Film. Für Kontrolle war reines durch Ameisensäure und Schwefelsäure erzeugtes Kohlenoxyd in die Apparatur eingeführt, unter Anwesenheit von flüssiger Luft zwecks Ausfrieren von Unreinigkeiten, und sein Hochfrequenzspektrum aufgenommen. Die viele starke Bande erstreckten sich fast gleichmässig von Rot bis ins weiteste Ultraviolett.

Die Literatur wurde für J o d m e t h y l f l u o r e s - c e n z und betreffende Anleitungen gut durchgesucht. Ein Vergleich zwischen seinem Absorptionspektrum (24 u. 25) und den bekannten Emissionslinien von verschiedenen Elementen zeigte die Möglichkeiten, dass Funken von Sn, Co, Ni, und eventuell Au und anderen Metallen, Fluorescenz vom ersten Elektronensprungniveau erzeugen könnten. Nach Rechnungen ähnlich denen für Aceton, würde man erwarten, dass ein Rot und Ultrarot Kontinuum vorkommen würde, und ebenfalls, ein diskretes Spektrum vom Zurückfall in den Grundzustand (ca. 50000 cm^{-1}). Wegen Mangel an Zeit konnte experimentelle Arbeit nicht weiter fortgeführt werden.

Herr Otto Stoll machte Untersuchung mit Zinnfunken im Dampfdruckgebiet 0,1 - 6 mm. an Jodmethyl, aber Zersetzung und Fensterbeschlagung verdarben die Versuche. Die gesamte Apparatur wurde Herrn Doktor Adolf Henrici übergeben, aber die Arbeit mit Aceton wurde noch nicht (Mai 1935) zu Beendigung gebracht. Weitere Versuche, vor allem mit Teslaerregung, lieferten bloss Kontinua.

Verhältnisse bei der Teslaerregung waren von meinen Nachfolgern näher studiert. Sie sind sehr kompliziert und schwer wieder herzustellen, aber scheinen bemerkenswert. Gerade jetzt ist die Arbeit wieder unter Fortsetzung und verspricht eigentlich Einiges von Interesse. Man studiert auch Jodmethyl mit Hochspannung.

Ich möchte hier meinen Dank an Herrn Professor Doktor G. Scheibe ausdrucken für seine Anregung zum Problem und sein grosses Interesse daran. Weiter hat Herr Diplom-Physiker G. Limmer mir öfters Rat und Hilfe gegeben, für die ich ihm herzlichen Dank schulde. Herr Doktor A. Henrici hat mir einen grossen Dienst geleistet, indem er die Apparatur und Fortsetzung der Arbeit so freundlich übernahm.

Mein Aufenthalt in Deutschland wurde durch den Travel Prize von dem California Institute of Technology und ein Stipendium des German-American Exchange Fellowship, unter Mitwirkung des California Institute ermöglicht.

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STUDIES OF THE NATURE AND REACTIONS OF OXIDIZED SILVER COMPOUNDS, ESPECIALLY IN NITRIC ACID

STUDIES OF THE NATURE AND REACTIONS OF OXIDIZED SILVER COMPOUNDS, ESPECIALLY IN NITRIC ACID.

Introduction

Studies of the nature and reactions of oxidized silver solutions have extended over a period of five years in this laboratory, involving the attention at various times of nine experimenters (Ref. 1), three being undergraduate and four graduate students. The final interpretation of a great deal of this work has been held up until the chemical kinetics of the spontaneous decomposition in nitric acid was better explained. The larger part of this paper will deal with experiments I have made attempting to unravel the complicated relationships existing in the decomposition, and the remainder will consist principally of correlation of these and further experiments I have made with observation of others in an attempt to formulate an explanation of the behavior of argentic silver.

An account of the general inorganic chemistry of argentic oxides and references to the literature on the subject will be found in the first of the series of articles, ''Argentic Salts in Acid Solutions'' (Ref. 2a), now being published by Prof. A.A.Noyes and co-workers. Only the more important observations will be mentioned here. Luther and Pokorny (Ref. 3) showed that the black solid obtained on anodic oxidation of silver nitrate or sulfate solutions yielded two definite potentials dependent on the extent of oxidation, ascribed to the presence of AgO and Ag_2O_3 respectively.

Jirsa and Jelinek (Ref. 4) produced oxides with identical behavior by the action of ozone on dry metallic silver and on Ag_2O.

Yost (Ref. 5) showed that the substance precipitated by $K_2S_2O_8$ from silver sulfate solution consisted of silver in the tervalent state. On recrystallizing from nitric acid several times and drying, the product corresponded to a state of oxidation in which one fourth of the silver was tervalent and three fourths bivalent. He also showed that the silver-catalyzed oxidation of chromic salts, ammonia, and vanadyl ion by peroxysulfate should be ascribed to an intermediate of tervalent silver. The role played by silver in this type of reaction was studied by Carman (Ref. 6), and the precipitated oxides were analyzed chemically and potentiometrically with results in accord with those mentioned above. Fluorine, lead dioxide, and bismuth pentoxide have also been used to oxidize silver compounds.

As is to be expected, the black or deep brown solution of the oxides in HNO_3 or H_2SO_4 is a powerful oxidizing agent, oxidizing rapidly hydrogen peroxide, oxalic acid, and thallous, chromic, cerous, and iodate ions. Manganous ion is oxidized partly to manganese dioxide, and partly to permanganate. In addition, these solutions undergo spontaneous decomposition with the evolution of oxygen.

J.L.Hoard found that silver nitrate in nitric acid was oxidized at a measurable rate by 3%--5% ozone, and made a preliminary study of it, the work being continued by K.S.Pitzer. These observations, interpreted in the light of results to be given here,

compose the paper of Ref. 2a. Article II of this series treats the state of oxidation in strong nitric acid (Ref.2b) and Article III (Ref. 2c) the electrode potential of bivalent silver in nitric acid solution.

Experimental Treatment

A. Analytical

a, $FeSO_4$ Method. The method developed by Hoard consisted of pipeting the nitric acid solutions of oxidized silver into standard ferrous sulfate reagent, presumably in large volume, and titrating the excess ferrous ion with standard permanganate. If the nitric acid is very strong and the reducing solution not in large volume, there is danger of introducing an error by nitrate oxidation of ferrous ion, and under certain conditions the ferrous ion may reduce the argentous ion to free silver, I found. This can be seen as a silky precipitate which is not oxidized quantitatively by permanganate if it has stood too long. It may not be best to use as an analyzing solution one of composition different from that in which the argentic ion is dissolved, because of danger of decomposition before reaction with standard reducing agent, but with reactions as rapid as this one, I doubt that this objection is serious.

I have treated all of Hoard's experiments graphically and find excellent internal agreement in the analyses. There is no reason to suspect that errors in analysis were excessively great even when the argentic ion was in 12 N HNO_3, unless the error is constant. For all subsequent work, however, one of the other methods outlined below was used.

b, $TlNO_3$ Method. At the time that the most accurate steady-state measurements were being made by Professors A. A. Noyes and Isaburo Wada, a method of analysis was required about which there

should be no doubt. It was desired that the reducer be either a solid which would dissolve rapidly in 15 N HNO_3 on reaction or a substance which would not react with the acid when made up in solution in it.

I prepared a small test eudiometer to ascertain if O_2 were given off during the reaction between argentic silver about 0.2 normal with the reducing agent at 0°. The eudiometer was filled with cold argentic solution in nitric acid and the analyzing reagent was introduced through a side arm under the solution. Rocking served to mix the reagents and any gas bubble was trapped in the upper portion. It was found that $Mn(NO_3)_2$ was unsatisfactory either in the solid state or as a saturated solution in 6 N HNO_3, for hydrated MnO_2 forming seemed to catalyze decomposition of the argentic ion with evolution of oxygen, a very small quantity of which could be seen easily. Solid thallous nitrate reduced the silver as rapidly as diffusion to the neighborhood of the solid could take place, and no gas was given off. Furthermore, qualitative tests showed that thallous ion reduced ozone satisfactorily.

A number of methods had to be tried before an accurate one could be found for analyzing thallic nitrate in the presence of thallous and silver nitrates in strong nitric acid. Ferrous sulfate did not react rapidly enough with thallic ion; the presence of nitrate made difficult the using of titanous sulfate; even after separation no sharp electrometric end-point could be obtained. Various methods involving oxidation of residual thallous ion with permanganate failed.

It was finally found necessary to neutralize very carefully the cold acid solution with conc. NH_4OH, filter off the precipitate of thallic hydroxide, dissolve in 1 N HCl solution, and titrate hot with standard potassium bromate solution, using the decolorization of methyl orange indicator as the end point. (Method of Zintl and Rienacker Ref. 7.) This was necessary to determine the amount of thallous ion occluded with the thallic hydroxide. The thallium was then reduced to monovalent form by SO_2 gas, the excess boiled out, and the titration repeated so that the total thallium could be determined. Careful tests indicated that the method was very accurate. The total silver present could be determined by precipitation of AgCl in the acidified filtrate from the thallic hydroxide separation. It was shown that the thallous chloride did not interfere. This essential method has served as the standard for all analyses of argentic silver, against which new methods may be checked.

c, As_2O_3 Method. In searching for a method which would be more rapid than the $TlNO_3$ one and applicable to both argentic silver and ozone, F.B.Stitt and A.I.Kossiakoff studies thoroughly a number of reducing agents. They found that a neutral solution of As_2O_3 was satisfactory. A known quantity was taken and the excess titrated with standard iodine after precipitation of the silver with chloride. However, this solution is not stable in nitirc acid, nor could it be used when the silver was in nitric acid more concentrated than about 5 N.

d, $Cr(NO_3)_3$-HNO_3 Method. At 25°, 6 N and stronger nitric acid solutions offer rates which are most accurately and conveniently measured. The method based on solid $TlNO_3$ as a reducing agent is far too tedious to allow rate of reaction to be studied extensively; the other methods described above are not completely reliable for acid of this strength. For safety I desired to make the reducing agent up in nitric acid of the same concentration as that in the sample being analyzed. At the suggestion of Prof. E.H.Swift, chromic nitrate was tried.

Approximately 5 ml. of 6 N HNO_3 containing 2 milli-equivalents (an excess) of chromic ion was taken. The argentic solutions in 6 N HNO_3 were decolorized instantaneously without gas evolution. Standard ferrous sulfate was added until the yellow from dichromate was decolorized in such a dilution that ferrous ion was not oxidized by the nitrate, and a back titration was made with standard permanganate. If the analyzing stock solution of $Cr(NO_3)_3$ was more than a day old, the color had faded from bright purple or green to a pale bluish-purple, and .02--.04 Ml. of .05 N $KMnO_4$ gave an easily detectable red color, which was corrected for with blanks. The titration takes very little time and gave all evidence of being exact.

J.T.Baker's 30 % C.P. chromic nitrate solution was diluted with NO_2-free nitric acid and distilled water to the desired concentration.

Several analysis-sets were made before an unsuspected error was discovered. A solution containing 5.0 ml. of the $Cr(NO_3)_3$-HNO_3 reagent and the same amount of acid as used in a typical analysis is colored pink by the first drop of $KMnO_4$.

If, however, a known quantity of $FeSO_4$ is added and then the back titration with $KMnO_4$ is made, more permanganate is used than is expected. This is caused by some impurity in the chromic nitrate reagent, perhaps by an NO- or NO_2-complex formed by reaction induced by light. The original $Cr(NO_3)_3$ free from HNO_3 does not react so in acid solution, nor does the HNO_3 alone. Continued bubbling of dustfree air does not decrease this end-point correction. The reaction of the reducing solution with $KMnO_4$ is exceedingly slow in the absence of Mn^{++} or Fe^{++} ions, and is not accelerated by Ag^{+} or Fe^{+++} ions. The product does not precipitate $PbCrO_4$ with lead nitrate under conditions of acidity and volume which gave a sensitive test with a small amount of added dichromate, and therefore is not due to oxidation of Cr^{+++} by permanganate.

The extent of reduction of permanganate (called the end-point correction) is greater in stronger acids; in one series, 5 ml. of $Cr(NO_3)_3$ in 4 N HNO_3 used up 0.39 ml. of 0.078 N $KMnO_4$, while that in 6 N HNO_3 used up .81 ml., that in 9 N, .98 ml., all preparations having been made up at one time and of approximately the same chromic concentration. The end-point correction increased perceptibly over weeks, although the solutions were kept in a closed cupboard.

In spite of the empirical nature of this correction, it could be applied with great accuracy. It could be determined concordantly by different methods and was independent of the manner of titration within the limits outlined above. (presence of Fe^{++} or Mn^{++} ion in appreciable quantities.) It depended only

on the quantity of chromic reagent taken, which was always 5.0 ml. for each analysis, and it did not change perceptibly during one run, lasting perhaps several days.

B. The Divalency of the Argentic Ion

The most direct proof that the argentic ion is divalent in strong nitric acid solutions is given in the following experiment of Prof. Noyes, called by him the solubility method. The complete details of the method and results are given in the article II of his series (Ref. 2b), and with his kind permission the results given below are taken from there. Most of the analyses were carried out by Kossiakoff and Coryell.

In strong nitric acid (15.2 N at 20°), it was found that silver nitrate is rather insoluble. If, however, a solution in contact with $AgNO_3$ crystals is ozonized, a great deal more silver is dissolved due to the formation of the argentic compound. This increase in solubility is to be correlated with the increase in oxidizing power of the solution over that due to ozone alone, both increases being large compared to the respective corrections. In practice, the ozone was blown out with a rapid current of carbon dioxide so the oxidizing power measured was due to argentic ion alone. Work was carried on at -5.8° to avoid decomposition as much as possible during this operation, and to favor as high a concentration of argentic ion as possible. Table 1 summarizes the observations and calculations.

Table 1

Solution	Atomic Wts. of Silver		Oxidation equivs.	
	In kg. soln.	Per kg. 15.2 N HNO_3	In kg. soln.	Per kg. 15.2 N HNO_3
Steady-State Mixture	0.3023	0.3193	0.2332	0.2463
Sat. $AgNO_3$ Soln.	0.0598	0.0604	0.0	0.0
Difference	0.2425	0.2589	0.2332	0.2463

Ratio of Oxidation Equivalent to Argentic Salt Concentration, referred to kg. of 15.2 N HNO_3: 0.951

The very careful work represented by this Table indicates that at the time of measurement each atomic weight of argentic silver could oxidize 0.951 equivalents of thallous nitrate, or had an average valence of 1.951. The departure of this number from 2.00 may reasonably be attributed to experimental error, to some decomposition occuring while the ozone was being swept out, and to the fact that the solubility of argentous nitrate may have been influenced by the appreciable concentration of argentic nitrate. No analysis has shown a value greater than 2.00 for the valence of argentic ion in solution. The evidence from electromotive-force (Ref. 2c) indicates that, at least in the main, the argentic ion is bivalent even in acid as dilute as 1 N HNO_3.

C. Anodic Oxidation of Silver

Preparation of Solution. Prior to this phase of the silver research, all investigators had prepared their solutions of argentic

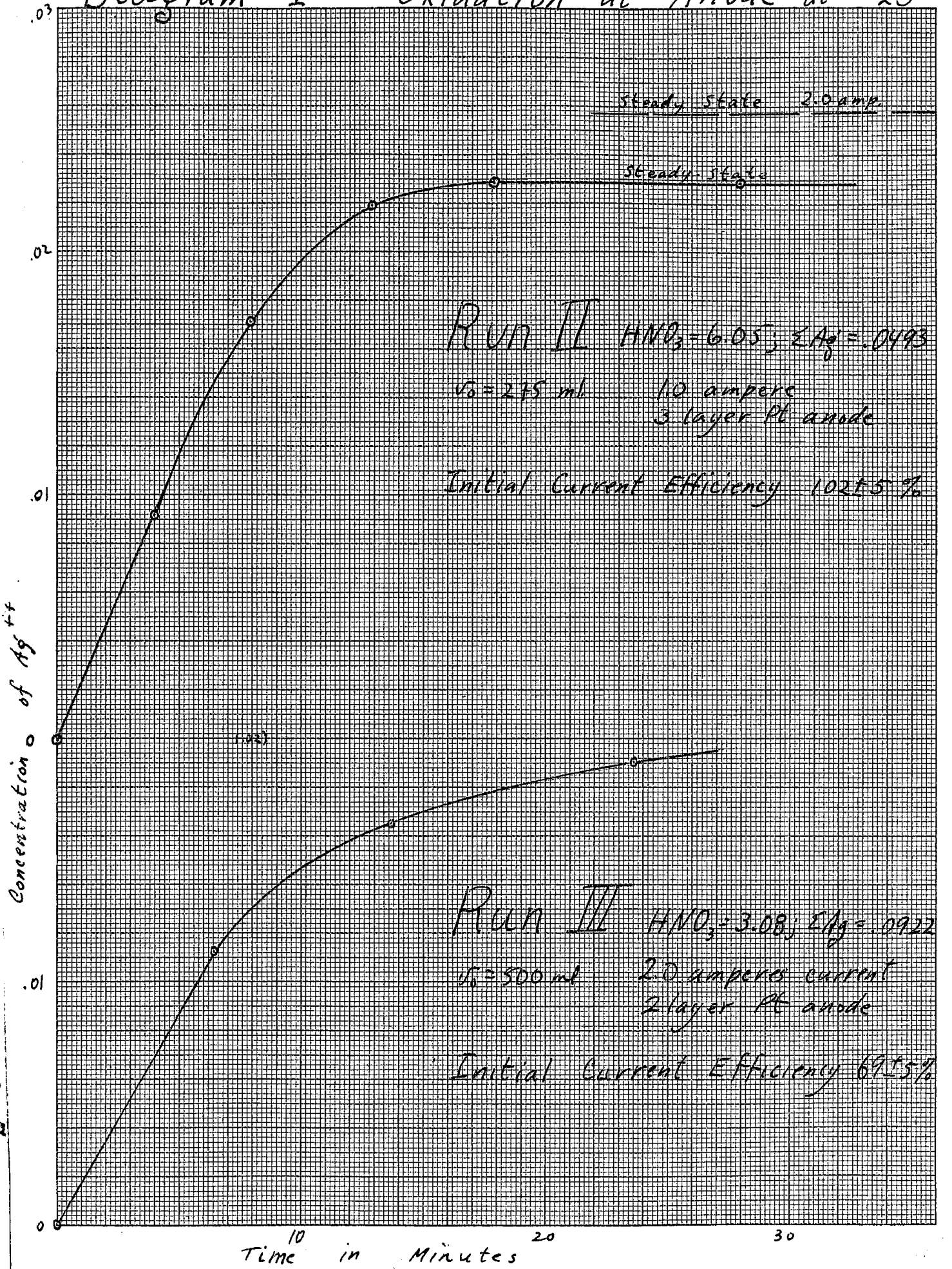
nitrate by the action of ozone, which is slow and requires much special apparatus. Potassium persulfate oxidizes silver nitrate rapidly, but it is impossible to separate the argentic compound from occluded or combined sulfate (Ref. 5a). A compound conforming to the formula Ag_7NO_{11} is prepared by anodic oxidation of 10% $AgNO_3$ solution, and it was shown by Jirsa (Ref. 8a) that boiling water decomposes this partly, leaving pure AgO. However, the easiest method of preparation, it was found, is to oxidize $AgNO_3$ of any desired strength in HNO_3, separating the cathode from anode by a porous cup or a U-arm.

In a small unglazed porcelain cup, about 23 mm. in diameter and 70 mm. deep, 2 N HNO_3 was placed with a Pt wire for anode. A large beaker held the anolyte stirred by the rotating three-layer smooth-platinum gauze anode, a thermometer, and a test-tube of ice for cooling. For oxidation at 0° cooling was attained by use of a bath with NH_4Cl -H_2O eutectic surrounding the apparatus. Oxidation was begun somewhat below the desired temperature for the final solution, the heat developed in internal resistance gradually warming the solution.

The preparation of solutions of argentic nitrate in HNO_3 is mentioned by Weber (Ref. 9).

Current Efficiency. Diagram 1 shows two curves for the concentration of argentic silver as a function of time, which are similar to corresponding curves for ozone oxidation. In curve II, the current efficiency is 100%, and therefore the rate of oxidation is independent of the argentous concentration, however, so

Diagram 1 Oxidation at Anode at ~25°



that a functional relationship existing between concentrations at the electrical steady-state (the flat portion of the curve soon attained) will be different than that for ozone. The horizontal line above indicates the approximate position of the steady state for a current of 2.0 amperes. In anodic oxidation the rate of increase of oxidizing power is inversely proportional to the volume, but the small correction for changing rate as each sample of 10ml. was withdrawn, was not applied.

For curve III a current density three times as great was used, and the acid concentration was lower initially, both effects probably lowering the current efficiency, which is calculated to be 69%.

At 0° with HNO_3 concentration of 2 N, current efficiency was frequently very low, and simultaneous formation of small quantities of ozone was sometimes noticed. In dilute acid one must always be careful about the possibility of precipitation of Ag_2O_3 or Ag_2O_3-AgO mixtures if the argentic ion becomes moderately concentrated. The emery-like grey solid may be removed by filtration, or by several decantations until no more forms.

Maximum Electrical Oxidation. It was found that the use of a U-tube to separate anode and cathode decreased internal resistance considerably. An apparatus with a connection about 10 mm. in diameter was made which fitted in a Dewar flask. The anolyte could be stirred vigorously with a stirring motor but no mixing between anolyte and catholyte took place.

About 50 ml. of 12 N HNO_3 approximately 0.08 f. in $AgNO_3$ was

electrolyzed for 45 minutes with 1 ampere current at -8°. Just as the current was shut off, 10 ml. of cooled $Cr(NO_3)_3$ in 9 N HNO_3 was added. This caused a surge of unreduced anolyte to fill the U-portion. The cathode was then tightly stoppered and the stirring of anolyte stopped, so that portions of it could be removed for analysis. Above the constriction of the U-tube the solution was a homogeneous mixture of chromic, dichromate and argentous ions so that the ratio of analysis for oxidizing power (dichromate) and silver would be the same as before the chromic reagent was added. (Unfortunately, a small amount of silver dichromate precipitated into the U-portion, removing relatively more oxidizing agent than silver and tending to make the results somewhat low.) The ratio turned out to be 0.95 in the best preliminary experiment. A preliminary experiment in 6 N HNO_3, 0.04 f. $AgNO_3$ with 1 ampere, indicated a ratio much less than 1.00 for the electrical steady-state.

Thus in strong acid the ozone results are corroborated for maximum oxidation, and in dilute acid it is difficult to oxidize as far because of the much more rapid decomposition rate. In this method, the correction for unoxidized silver cannot be applied as it cannot be determined; therefore the average valence of all forms must be raised above 2.0 to indicate tervalent silver. However, in stronger nitric acid, this method may be applied to solutions in the presence of argentous nitrate as with the ozone method.

Oxidation of Cyanide. Anodic oxidation in 6 N HNO_3, 0.06 f. $AgNO_3$, with 0.5 amperes, was carried on for several hours at about

35° in the presence of freshly precipitated AgCN. The black solution which had formed before the addition of the solid was slowly decolorized and remained colorless. The decolorized solution produced no iodine with starch-iodide solution, nor gave any other evidence of the presence of an argentic complex analagous to nickelocyanide (unstable in acid) or cobalticyanide (very stable.)

D. The Rate of Reduction

Manipulation. A solution of argentic nitrate of the highest concentration obtainable without danger of precipitating Ag_2O_3 (dependent principally on the acid) was easily to be obtained in from 5 to 15 minutes by anodic oxidation, its temperature being within 0.5° of any desired one. It was then placed in a 500 cc. g. s. bottle and shaken vigorously in the thermo-stat for about 5 minutes. after which a sample was withdrawn and pipetted into the $Cr(NO_3)_3$ in HNO_3 of closely the same strength, the time being measured when half the solution had drained from the pipet. After about 5 minutes, a second sample was withdrawn and both analyzed. Time intervals were then chosen at lengthening time intervals so that roughly the same percentage decrease in concentration would occur in each interval, samples amounting to 10.0, 25.0, 50.0 and sometimes 100.0 ml. being taken. In the usual run, from 9 to 14 samples were analyzed, the concentration of Ag^{++} dropping from initial values of from .007 to .08 to values of from .0005 to .002 normal. In Run VIII a three-thousand-fold change in rate was followed over 3 days with 14 samples.

The experiments were made in the diffuse light of the laboratory,

no special precautions being taken to protect the solutions from exposure. Qualitative evidence indicates that they are somewhat light-sensitive, as seems reasonable for such intensely colored unstable solutions. A photochemical decomposition should be much more in evidence in the later portion of the run where the pure thermal rate is slow. It can hardly be of appreciable effect, however, for no difference is to be noticed between runs made in day-time and night-time, and in this concentration range the decomposition followed a simple law very closely.

Before any rates of decomposition were observed, all the observations made by Stitt and Kossiakoff in six decomposition-runs at 0° in 2.00, 2.68, and 3.73 wt. normal HNO_3 were analyzed graphically to determine the functional dependence on concentrations by the methods described below. Three runs of Hoard in nitric acid, 2.0, 6.0, and 12.0 N, were of value for deducing the argentic dependence at 25° where it was, without much question, a quadratic one. At 0° the dependence was extremely complicated, in more concentrated argentic solutions seemingly fourth power, but in dilute solutions perhaps a transition between fourth power and second. At 0° an inverse argentous dependence was noted.

For the sake of directness, the decomposition was studied first at 25.0°; in all, sixteen different runs were made in 3.1, 6.1, and 9.4 N HNO_3 (by volume), the effect of ionic strength being tested by making the most dilute acid solution 3.0 molal in $NaNO_3$ to make the total ionic strength 6.1. After the nature of the reaction was fairly well understood, seven runs were made at 0.0° in 2.13, 3.70, and 7.60 wt. normal HNO_3 (resp. 2.00, 3.30 and 6.13 vol. normal)

to furnish any additional information, to calculate the Arrhenius heat of activation, and to correlate constants with those of previous workers' runs.

Treatment of Results. It was found fully as important to make the plots of the decomposition rate and the calculations very carefully as to make the analyses with the maximum accuracy, because of the numerous complications the reaction kinetics presents.

Ordinarily concentrations, c, observed with successive samples were plotted against time, t, on such a scale that 2 minutes were represented by 0.1 inch with suitable choice of ordinate-scale for concentrations. When the reaction proceeded longer than 600 min., a second curve which overlapped the first considerably was used for the final portion to give more accurate treatment of the slope which had become so small. In general, curves carefully plotted using a spline showed a fairly high degree of consistency indicating the absence of erratic errors.

For cases where the time interval began with 5 min. and lengthened out to a day or more, it was found convenient to plot c against $\sqrt{t + 20}$ to give a better curve. The slope of the curve divided by $2\sqrt{t + 20}$ gives the desired dc/dt. Adding a small time, say 20 min. to t sidesteps the occurence of a flex in the very early portion of the curve, between the first two points.

The slope of the decomposistion curve (dc/dt) is computed from small secants at convenient intergral values of the argentic concentration. In spite of great care, these slopes are hardly reliable to more than 10% due to inherent difficulties in measurement and irregularities in drawing the original curve. Sometimes as a check

these slopes were plotted against the argentic ion concentration to which they are quite sensitive, and grosser irregularities could be smoothed out. Here could be applied the first criterion: this curve must fall to zero horizontally. This is true for any decomposition which proceeds according to any positive power of argentic concentration greater than 1. This is often of assistance in interpreting decomposition rates at extremely low argentic concentrations were experimental error is large, as must be done so carefully at 0°.

Analysis of Observations

A. Kinetics of the Decomposition

Effect of Argentous Ion. The first factor to eliminate is that due to the unoxidized silver. At a given acid concentration (sensibly constant during the period of decomposition), two runs may be compared at the same concentration of argentic ion; under these conditions they differ only in argentous concentration. If the rate of decomposition is inversely proportional to the argentous concentration (as preliminary observations indicated), the product of the observed slope and the prevailing argentous concentration will be constant from solution to solution at a given argentic concentration. In Table 2a the values for the product are listed at integral values of concentration of Ag^{++} for three sets covering a total range of variation in monovalent silver of five-fold at 25° and twenty-fold and three-fold at 0°.

If the assumption that the rate of decomposition is inversely proportional to the prevailing argentous concentration is true, then the figures in any one column should be equal. Values in parenthesis are subject to greater error in observation. It is true that there is a general spread of the value in any column at either temperature, larger than may be explained by slight variations in HNO_3 concentration, but there is no systematic variation commensurable with the large variations in total silver, (and monovalent silver, $\Sigma Ag - Ag^{++}$) which are under consideration.

Table 2a. Product of Rate of Decomposition and Argentous Ion Concentration

Av. HNO_3, 9.3_7 v.n.; t 25.0°; Product in 10^{-6} mol^2 $liter^2 min.$

$\frac{Ag}{Ag}$	60	50	40	30	20	15	10	6	4 x 10^{-3}
0.0905 v.n.	--	--	(47)	22	7.8	4.3	1.8	0.67	0.35
0.181_5	99	61	36	20	8.2	4.6	2.0	.70	(.35)
0.315_4	95	58	45	17	7.4	3.9	2.4	.65	(.46)

Av. HNO_3, 3.3_1 v.n.; t 0.0°; Product in 10^{-6} mol^2 $liter^2 min.$

$\frac{Ag}{Ag}$	20	8	6	5	4	3	2 x 10^{-3}
0.0168 v.n.	--	---	(0.67)	0.31	0.13	0.046	(0.015)
0.0510		(1.2)	.43	.33	.16	.049	(.025)
0.247	26	0.91	.31	.15	.10	(.059)	---

Av. HNO_3 6.13 v.n.; t 0.0°; Product, 10^{-6} mol^2 $liter^2 min.$

$\frac{Ag}{Ag}$	16	14	12	10	8 x 10^{-3}
0.0386 v.n.	1.02	0.69	0.40	0.24	0.15
0.0872	.50	.32	.23	.14	.10

Table 2b. Product of Rate of Decomposition and Square of Argentous Concentration

Av. HNO_3 6.13 v.n.; t 0.0°; Product, 10^{-9} mol^3 $liter^3 min.$

$\frac{Ag}{Ag}$	16	14	12	10	8 x 10^{-3}
0.0386 v.n.	23	17	10.5	6.9	4.6
0.0872	35	23	17	10.8	7.9

At 25° there seems to be little question about this conclusion, but at 0° the constant may be falling off with increasing argentous ion in more concentrated solution. To test this possibility more quantitatively, Table 2b is presented where the product of observed slope and the square of the argentous concentration is given for the series of argentic concentrations in 6.13 N HNO_3, which seemed to show the greatest deviations. In this case, the values listed seem to rise with argentous concentration almost as much as they fell in Table 2a. This point will be discussed more thoroughly in the next subdivision.

It seems quite probable that throughout the whole range of decomposition, the rate of decomposition is within (rather large) experimental error inversely proportional to the argentous concentration prevailing.

Effect of Argentic Ion. Inspection of Table 2a shows that the argentous-rate product falls rapidly off with decreasing argentic concentration. Thus, in the first series at a concentration of 20 milliformal, the value is roughly 8, and at argentic concentration half as great, it has fallen to 2, one fourth as great. In 6.1 acid, (not tabulated for 25°), it falls from about 35 to 6.5 in the same range, a decrease of somewhat over five-fold. These would indicate roughly second-power dependence, although deviations occur at the higher argentic concentrations.

In the first series at 0° this dependence holds only in

in extreme dilution. Decreasing the argentic ion from 3 to 2 mf. lowers the product a little over two-fold. On the other hand, a change of 2.3 fold being expected for both cases.

Because of the evident complications presented, it is not practical to calculate rate constants from point to point; a graphical method, then, offers the best procedure available. For example Diagram 2 contains plots for three runs made at 9.4 $\underline{N}$ HNO_3 at 25° where ordinates represent the rate of decomposition in milli-equivalents per minute and abscissas represent the function $\frac{(Ag^{++})^2}{(Ag^{+})}$ in milli-formula-weights per liter. If the decomposition depends on this function of the concentration, then the plots will be straight lines passing through the origin; the curves must pass through the origin in any case, for rate of decomposition will be zero when the concentration of argentic ion is zero.

As may be seen, the curves plotted for this concentration-range are quite accurately linear, and furthermore the slopes, corresponding to the second-order constant, k_2, are closely the same.

When the runs made in 6.1 or 3.1 $\underline{N}$ HNO_3 are treated in the same way, as in Diagram 3, the same strict conformity to linearity is not observed, except perhaps in the neighborhood of the origin, representing the advanced stage of the decomposition where argentic concentration is quite small. On the basis of larger scale plots of these lower portions of the curves, the straight lines have been drawn in which the curves

Diagram 2. SECOND-POWER FUNCTION 25°

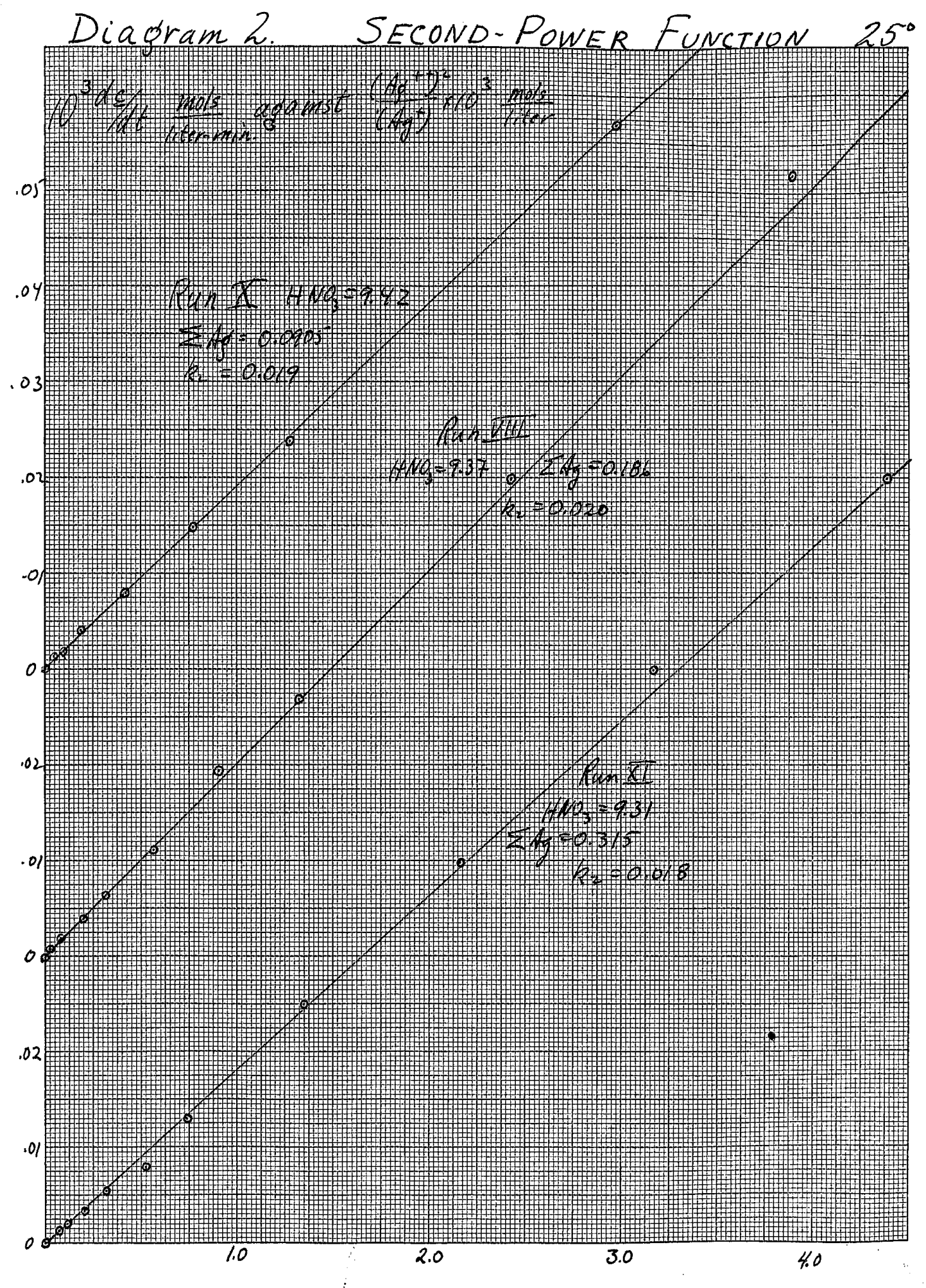


Diagram 3 SECOND-POWER FUNCTION — BORDERLINE CASES

$10^3 \frac{dc}{dt}$ $\frac{mols}{lit.min.}$ against $(Ag^+)^2 \times 10^3$ $\frac{mols}{liter}$

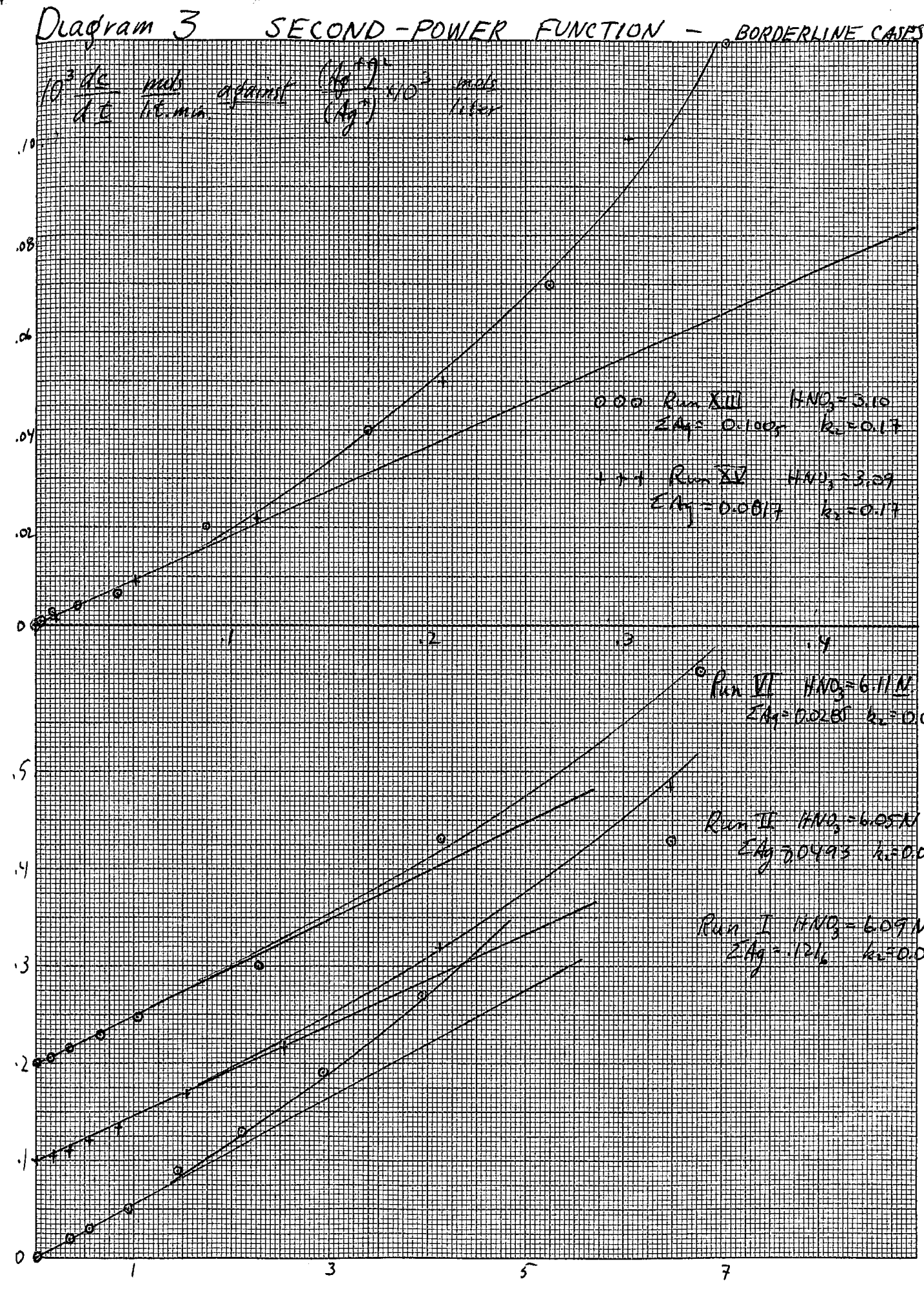
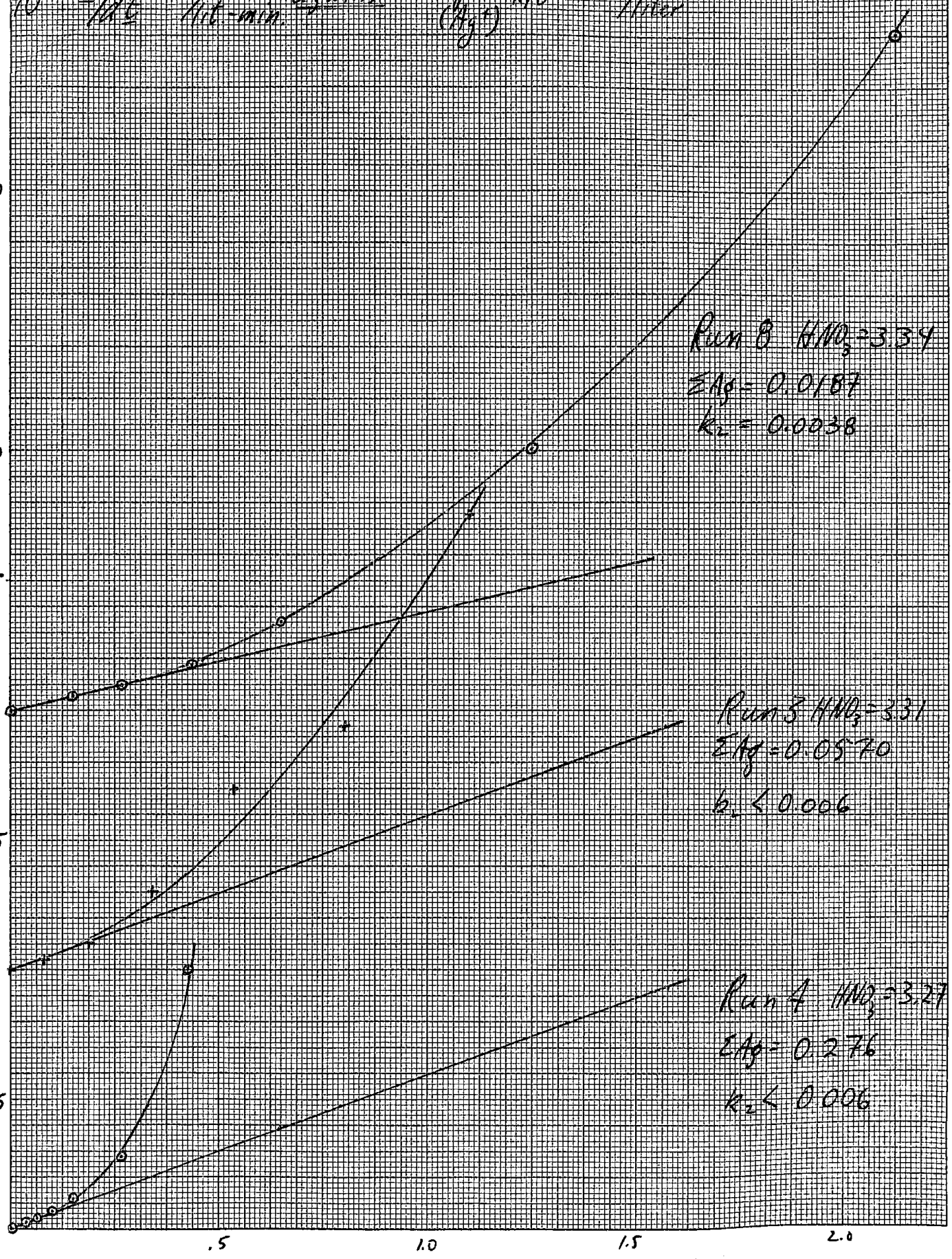


Diagram 4 Second-Power Function 0°

$10^6 \frac{dc_{Ag}}{dt}$ mols/lit-min. against $\frac{(Ag^+)^2}{(H_3O^+)} \times 10^3$ mols/liter



seem to approach asymptotically as decomposition of the argentic solutions nears the completion and the rate of decomposition falls off to zero.

This effect is even more strikingly shown in Diagram 4, consisting of three runs in 3.3 N HNO_3 at 0°. Indeed, deviations from the second-power law persist so long that it is extremely difficult to establish the second-order constant accurately. For Runs 3 and 4 the line represents the maximum permissible second-order reaction constant.

It was found that the deviations from the second-power law gives a straight line when plotted against the function $\frac{(Ag^{++})^4}{(Ag^{+})}$, as has been done for these three same runs at 0° in Diagram 5. In any run the argentous concentration varies at most only about 25%, so that it is difficult to determine from one curve if the argentous dependence is inverse first power or inverse second power. The broken curve in Run 3 of Diagram 5 indicates the trend of the rate of decomposition if correction is not made for the simultaneous occurence of the second-power decomposition. The line is essentially straight at higher argentic concentration but does not extrapolate through the origin. At 0° the fourth-power decomposition is in general predominate, usually overwhelmingly so.

Diagram 6 indicates the fourth-power dependence at 25° of that part of the decomposition not accounted for by second-power decomposition for all cases where argentic ion was concentrated enough. For these cases the constants k_2 could be determined as accurately as is indicated in Diagrams

Diagram 5 FOURTH-POWER FUNCTION 0°

$10^6 \Delta \frac{dc_A}{dt}$ $\frac{\text{g-mols}}{\text{lit.-min}}$ ordinate $10^9 \frac{(\Delta p^{1.5})^4}{(V_g)^3}$ $\left(\frac{\text{mols}}{\text{lit}}\right)^3$

Run 8 $HNO_3 = 3.34$

$\Sigma k_g = 0.0187$

$k_2 = 0.0038$

$k_4 = 400$

Run 3 $HNO_3 = 3.31$

$\Sigma k_g = 0.0510$

k_2 assumed 0.006

$k_4 = 200$

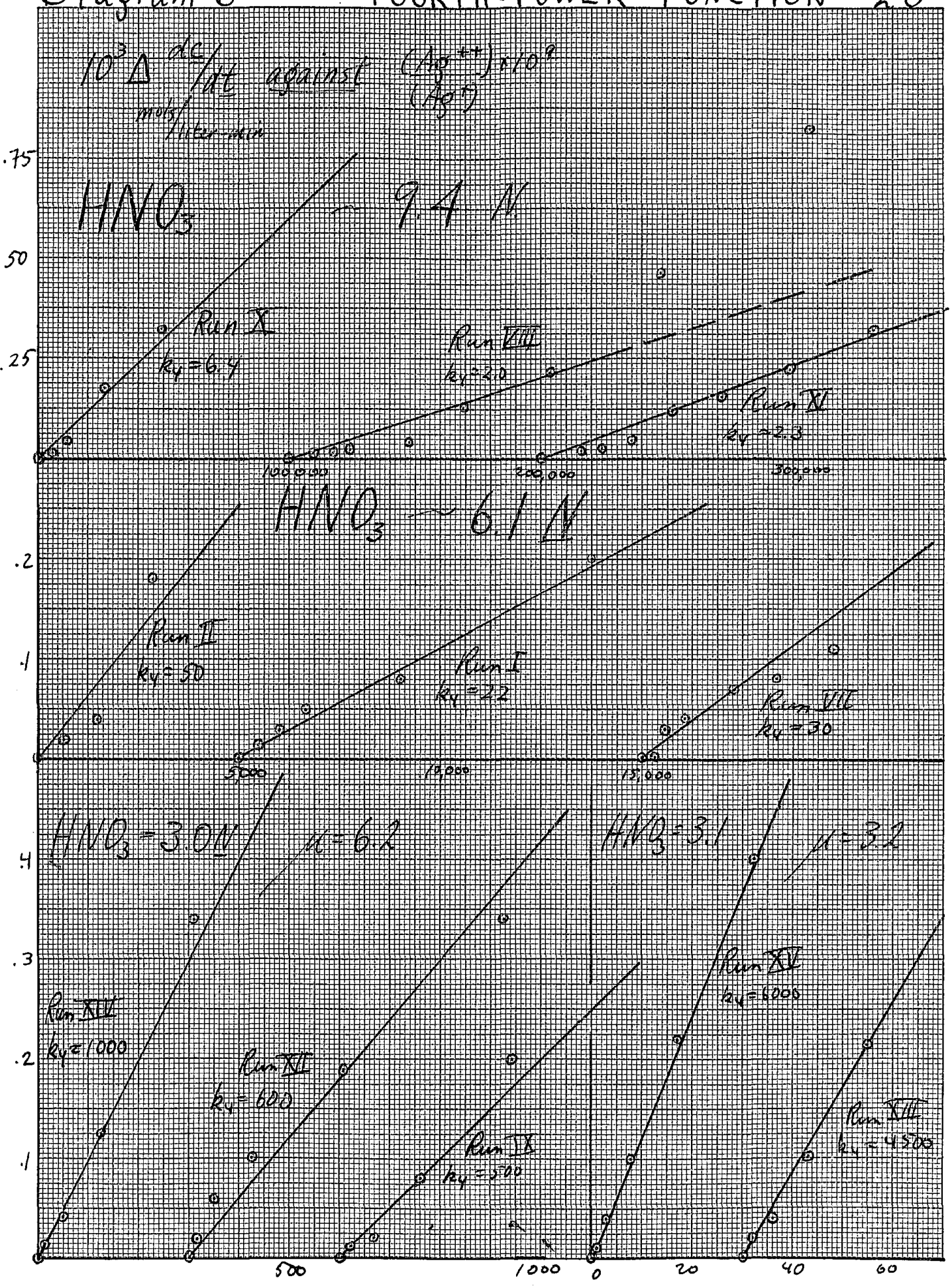
Run 7 $HNO_3 = 3.27$

$\Sigma k_g = 0.247$

k_2 assumed 0.006

$k_4 = 150$

Diagram 6 — Fourth-power function — 25°



2 and 3 by the linear portions of the curves. In most cases in Diagram 6 the dependence is reasonably well established as linear with the fourth-power function indicated; at 0° there is no question at all about the validity of this function.

Constant k_4 represents the slope of the line representing rate of decomposition (corrected for second-power) plotted against $\frac{(Ag^{++})^4}{(Ag^{+})}$. There have also been calculated constants k_4' which represent the slope obtained from the rate plotted against $\frac{(Ag^{++})^4}{(Ag^{+})^2}$, These constants differ but ten or twenty percent generally from the product of k_4 and ΣAg. In Table 3 are represented all the reaction rate constants for a given acid concentration derived graphically from fifteen runs made at 25°. Column 1 gives the run number; 2, the acid concentration; 3, the total silver; 4, the ionic strength, $NaNO_3$ being added in one series; 5, the constant for second-power decomposition, K_2; 6, the arbitrary weight for the determination, roughly indicating the number of points which determined the line; 7, constant k_4; and 8, constant k_4', the latter two being fourth-power constants with different argentous dependence assumed; and 9, the weight for the two constants.

Table 4 gives a collection of the constants for eight runs made at 0°, where the columns are the same as for Table 3.

Table 3. Rate Constants at 25.0°

Run	HNO_3 v.n.	ΣAg	ΣNO_3	k_2	Wt.	k_4	k'_4	Wt.
XV	3.09	0.081_7	3.17	0.17	3	6000	470	4
XIII	3.10	$.100_5$	3.20	.17	4	4500	440	3
III, IV	3.08	$.085_2$ $.201_1$		.17	4	---	--	-
		(Weighted Mean		.17		5400	460)	
XIV	3.01_5	.0912	6.14	.17	3	1000	88	3
XII	3.02	.0915	6.15	.15	5	600	52	3
IX	3.02	$.161_4$	6.23	.11	6	500	84	3
		(Weighted Mean		.14		700	76)	
VI*	6.11	.0285		.043	5	~120 ?	2	1?
II*	6.05	.0493		.046	4	50	1.6	3
I*	6.09	$.121_5$		.055	4	22	2.4	4
VII	6.10	.201		.085	6	30	4.0	4
V*	6.00	.503		.052	7	--	--	-
		(Weighted Mean		.058		40	2.6)	
X	9.42	$.090_5$		.019	7	6.4	0.33	4
VIII	9.37	$.181_5$		.020	9	2.0	.34	3
XI	9.31	$.315_4$		.018	7	2.3	.59	5
		(Weighted Mean		.019		3.6	.45)	

* Corrected for Cr^{+++} end-point later, correction from indirect evidence.

Table 4. Rate Constants at 0.0°

Run	HNO_3 v.n.	≤Ag v.n.	k_2	Wt.	k_4	k_4'	Wt.
6	2.00	0.0183	0.011	2	590	8.2	4
5	2.00	.0281	.013	3	680	16.	3
2	3.13	.0872	~.004	1	350	30	3
8	3.34	.0168	.0038	4	400	7.2	3
3	3.31	.0510	<.006	2	200	9.6	5
4	3.27	.276	<.006	1	150	33.	6
7	6.13	.0478	.0013	3	11	0.28	5
1	6.13	$.108_0$	.0010	4	3.8	.28	4

We are now in a position to consider the relative agreement of the values k_4 and k_4'. At 25° constants k_4 at a given acid concentration fall off somewhat with increasing total silver. However, constants k_4' in general do not show much better agreement. In fact, the weighted average deviation (that is, the summation of the deviations each weighted as the run is weighted and divided by the total number of weights) for k_4' is only approximately half as great as that for k_4. In view of the great variations in the fourth-order constant, this may not be very significant.

At 0° the constants k_4' are very much more erratic than those at 25°, and it is here that one should expect the greatest accuracy in determining the constant. This matter is by no means completely cleared up, however, as a comparison of constants for 3.3 N HNO_3 would indicate. More experimental work should be done at 0° to ascertain the cause for the large deviations in the constants, for the consideration of the plot for a given run leads one to expect much greater trustworthiness of the constants. (See Diagrams 5 and 6).

We shall provisionally assume that the argentous dependence is inverse first-power for both functions representing decompositions of the solution proceeding simultaneously according to the second and fourth powers of the argentic concentration respectively.

Effect of Acid and of Ionic Strength. Considering the constants obtained for the work at 25° in Table 3, it is seen that k_2 is reasonably constant at one acid concentration. In 3 N HNO_3 doubling the ionic strength by the addition of $NaNO_3$ causes k_2 to decrease about 20%. Doubling the acid decreases the constant about three-fold, and increasing it from 6N to over 9 N causes approximately three-fold decrease.

At 0° increasing the acid by a factor of 1.6 (from 2.0 to 3.3) causes k_2 to fall about three-fold. Going to 6.1 N HNO_3 causes a change of about four-fold.

Although the experiments are not conclusive as to the hydrogen-ion dependence of k_2, it seems to vary inversely as the square.

At 25°, k_4 decreases very rapidly with both ionic strength and acid concentration, falling off roughly ten-fold at 3 N acid on doubling the ionic strength and falling off roughly ten-fold at ionic strength 6 on doubling the acid. Another ten-fold change is worked by increasing acid from 6 N to 9.4 N.

The changes at 0° are not as great in more dilute acid. Going from 2.0 N acid to 3.3 N decreases k_4 about three-fold. However, going from 3.3 N to 6.1 N decreases it roughly forty-fold.

That the fourth-order constants are not more reproducible is a little disquieting. This capriciousness might rest upon some property of solid silver oxides due to hydrolysis, but it observable up to 9 N HNO_3 at 25°. However, it is hard to see how, in the presence of any solid catalyst, that dependence on Ag^{++} could be so clear cut in any run. It is not out of the realm of possibility that both of the assumed decompositions are very sensitive to impurities. Stock C.P. $AgNO_3$ from three different manufacturers was used without further purification. The same porous cup was used for all anodic oxidations, and had been used at one time for oxidation of $PbNO_3$ and HNO_3. The nitric acid used was of C.P. quality, without further purification.

In summary of the concentration dependence of the decomposition of solids of argentic nitrate, it seems justifiable and probably necessary to express the rate of decomposition at a fixed acid concentration by the following expression:

$$\frac{-\,d\,(Ag^{++})}{d\,t} = k_2 \frac{(Ag^{++})^2}{(Ag^{+})} + k_4 \frac{(Ag^{++})^4}{(Ag^{+})} \qquad (1)$$

where k_2 seems to vary inversely with the square of the acid concentration, and decrease slightly in ionic strength, and where k_4 varies inversely with some high power of the acid concentration and decreases greatly with increase in ionic strength.

Fluoride Complex. In order to see if a complex with hydro-fluoric acid forms, a decomposition run was made in 6 N HNO_3 in the presence of HF. The concentrations for the run were:

Ag,= 0.0771, HNO_3 = 6.12, HF = 1.13, t = 25.0°

The reaction was carried out in a paraffin covered vessel. The initial argentic concentration was not high enough to allow observation of fourth-order decomposition, but k_2 turned out to be 0.080, approximately what is found in the absence of HF. Thus no stabilizing complex with HF is formed. (Compare P. 13).

Correlation with Work of Previous Observers. The same type of dependence on argentic and argentous concentrations is observed in the six runs made at 0° by Stitt and Kossiakoff, as my graphical analyses show. However, the absolute value of the rate constants are somewhat different, deviations at the same acid concentration being about the same. In 1.88 v.n. HNO_3 the value of k_2 for the run is about half as great as the mean of those in Table 4 for 2.00, and k_4 is only about one third as great. In 3.34 v.n. HNO_3, the mean of three values of k_2 is

about as large, but k_4 is only about one third as great.

Hoard made three runs at about 24°, the constants of which are in fair agreement with those of Table 3. Only two of the runs made by Pitzer at 0° may be compared; one in 1.78 N HNO_3 gives a k_2 of 0.017, the other in 1.78 N HNO_3 and 1.78 N $NaNO_3$ gives $k_2 = 0.0085$.

B. Mechanism of Decomposition

Second-Power Reaction. Consider the differential equation (1) given on P. 28. The fact that the rate of reaction may be expressed quite accurately as the sum of two terms, and not as a function which approaches asymptotically either of two functions in different ranges of concentrations, indicates that two decompositions occur simultaneously.

In the second-order decomposition, the pressure of argentous ion concentration to the inverse first power suggests that an equilibrium is involved in which an argentous ion is formed. If one of the products of this (rapid) equilibrium reacts with a measurable rate, the argentous ion would act as inhibitor. The simplest case would be the dismutation (reaction of two molecules of a substance involving oxidation of one and reduction of the other) of bivalent silver to some form of tervalent silver and monovalent silver. The existence of tervalent silver has been shown in oxides, and its existence, at least as an intermediary has been assumed from reaction kinetics of ozone and persulfate oxidations (Ref. 2a and 5). If this trivalent form of silver undergoes unimolecular or

pseudo-unimolecular decomposition, the kinetics would be represented by the following equations:

$$2\ Ag^{++} \longrightarrow Ag^{+} + Ag^{III}. \qquad Ag^{III} = K\frac{(Ag^{++})^2}{(Ag^{+})}\ ,$$

rapid equilibrium. (2)

$$Ag^{III} \longrightarrow \text{Products.} \qquad \text{Rate} = k_1 K \frac{(Ag^{++})^2}{(Ag^{+})}\ . \qquad (3)$$

If it be further assumed that the tervalent silver is hydrolyzed to the form AgO^{+}, as would be quite probable, the equilibrium constant and the rate equation will contain (H_2O) in the numerator and $(H^{+})^2$ in the denominator, giving the desired functional dependence on measure concentrations.

There is practically no other possibility for this equilibrium, unless hydrogen peroxide or pernitric acid are among the products. To produce a peroxy-compound, two atoms of bivalent silver are required and two argentous ions would be formed, which would take their place in the denominator. The peroxy-compound decomposing would then have to react with the argentous ion to give the experimentally observed rate dependence; this could only be assumed on the basis of a highly questionable reaction.

We must now inquire into the decomposition of the tervalent silver. The reaction:

$$AgO^{+} \longrightarrow Ag^{+} + O. \qquad (4)$$

would be very highly endothermic, and therefore atomic oxygen will not be formed. No simple mechanism except:

$$AgO^{+} + H_2O \longrightarrow H_2O_2 + Ag^{+}. \qquad (5)$$

can be adduced. One AgO^{+} can form ozone only from O_2, and such a reaction is contrary to fact because ozone is not formed during

decomposition, and will also be shown to be energetically impossible. Reaction (5) would give the same over all dependence as:

$$Ag^{+++} + 2\ OH^- \dashrightarrow H_2O_2 + Ag^+ \qquad (6)$$

involving unhydrolyzed tervalent silver. Either would be followed immediately by the following reaction, observed to be very rapid:

$$H_2O_2 + 2\ Ag^{++} \dashrightarrow O_2 + 2\ Ag^+ + 2\ H^+ \qquad (7)$$

so that the presence of hydrogen peroxide could never be detected.

There seems to be little doubt that H_2O_2 is an intermediate in the decomposition and that reaction (2) followed by (5) or possibly (6) represents the mechanism. This has been discussed by Prof. Noyes (Ref. 2a).

On the basis of the Brönsted theory, (Ref. 15) reaction (5) would be little affected by ionic strength, the total effect coming from secondary salt-effect from reaction (2). Including the hydrolysis, the effect would amount to a decrease in $\log_{10}k_2$ proportional to $2\sqrt{\mu}$, which is very large. However, it is impossible to apply such a law to such concentrated solution as we have here. It is significant that the direction of the deviation is correct. Reaction (2) without hydrolysis followed by reaction (5) gives exactly the same calculated dependence.

Fourth-Power Reaction. If the fourth-power decomposition were proportional to the inverse square of the argentous concentration, it could be admirably explained by the following slow reaction:

$$2\ AgO^+ \dashrightarrow O_2 + 2\ Ag^+. \qquad (8)$$

However, it seems that the argentous dependence is only inverse first power. This would indicate that only one atom of tervalent silver is involved. The high inverse acid dependence suggests that the reactants are highly hydrolyzed or that OH^- is one of the reactants. The reaction:

$$AgO + 2\ Ag^{++} + H_2O \longrightarrow O_2 + 4\ Ag^+ + 2\ H^+ \qquad (9)$$

accounts formally for all except the hydrogen ion dependence, but involves a collision between three positively charged ions, two with a charge of two. Moreover the total Bronsted dependence of k_4 in ionic strength would predict an increase in $\log_{10} k_4$ proportional to $6\sqrt{\mu}$.

But reaction of hydrolyzed products:

$$AgO^+ + 2\ AgOH^+ \longrightarrow 3\ Ag^+ + H_2O + O_2 \qquad (11)$$

predicts an inverse fourth-power hydrogen ion dependence and, by reducing the charge on the critical complex, predicts a decrease of $\log_{10} k_4$ proportional to $\sqrt{\mu}$. Assumption of further hydrolysis would make a steeper calculated dependence in the desired direction. However, such conclusions can be only of qualitative significance.

It is not possible to explain formally the fourth-power decomposition by considering that reaction (7) (by which H_2O_2 is destroyed) proceeds slowly; the only effect would be the building up of larger quantities of H_2O_2.

C. Temperature Dependence of the Rates.

In 6.1 HNO_3, k_2 increased from a mean of 0:0011 at 0° to

0.058 at 25° or 53-fold; in 3.3 N HNO_3 the value at 0° is about .004, and the interpolated value at 25° for this acid is 0.15, representing a 38-fold increase. In approximately 12 N HNO_3 Hoard made runs at about +0.5° and 24°; calculations of his observations indicate an increase in k_2 from 0.00015 to 0.0086, or 57-fold, which yields an increase of about 70 fold when calculated over at a 25° increase in temperature.

It seems surprising that the temperature coefficient should change so with the medium, factors for a 10° change in the range observed for 3.3 N, 6.1 N, and 12 N being respectively 4.3, 5.0, and approximately 5.6. The value for 6.1 N acid corresponds to an Arrhenius head of activation of 26,000 cal., and the other two being respectively 6% higher and 11% lower.

For 6.1 N HNO_3 k_4 increases from a value of approximately 7 to one of 40 or only about 5.7-fold, that is, 2.0-fold for a 10° increase in temperature. For 3.3 N HNO_3 the weighted mean for k_4 is 220. Interpolation from a curve of log k_4 against HNO_3 gave 3700 as an approximate value for 3.3 N HNO_3 at 25°, or 17-fold greater, 3.1-fold greater for 10° rise in temperature.

The great dependence of k_2 on the temperature is to be expected from the complicated nature of the reaction and the presence of an equilibrium. The much smaller dependence of k_4 on the temperature is probably due to effects of various equilibria and their heats which must be involved. The fact that the two reactions differ so greatly in temperature dependence aids in their separation: at 25° the decomposition is predominately due to the second-power reaction, and at 0° to the fourth-power.

D. Applications of the Decomposition Kinetics

Oxidation by Ozone. When the curve representing concentration of argentic silver against time of treatment with Ozone is plotted for ozone oxidations, one is immediately impressed by the fact that the curve in its initial portions is quite closely linear; however, when about three quarters of the maximum attainable argentic concentration has been attained, the curve bends over sharply and soon becomes level, indicating that the steady-state has been attained.
Six of such oxidations were observed by Stitt and Kossiakoff and the prevailing ozone concentration in solution was observed each time an analysis was made for argentic ion. They also observed the rate of decomposition of solutions of, in general, identical composition.

I have taken their curves for the oxidation, and measured the net rate of oxidation from the slopes. Then to this is added the observed rate of decomposition of the same solution. This sum, divided by the existing ozone and argentous concentrations gives the rate constant for the ozone oxidation (k_o) and the values remain remarkably constant.

Even more striking is the fact, that the rate of decomposition can be extrapolated by means of equation (1) using the mean of constants calculated from their decompositions and the corrected constant of oxidation from this calculation remains constant even when the steady-state has been attained. In other words, the ozone oxidation and steady-state measurements indicate that this treatment gives correct results even on considerable extrapolation.

The Electrical Oxidation. We could use the same line of attack on the rate of electrical oxidation if the current efficiency remained constant, for then in the steady state rate of oxidation would equal rate of decomposition.

Referring to Run II, as shown in Diagram 1, it is seen that in the steady state, Ag^{++} = 0.0228, and Ag^{+} = 0.0265. Using the mean constants from Table 3 for 6 N HNO_3 at 25°, the calculated rate of decomposition due to the second-power reaction is 1.14 milli-equivalents per liter per minute, and that due to the fourth-power reaction is 0.41, a total of 1.55 m. equ. per min. A current of 1.0 amperes was used, and the volume in the steady state is 0.225 liter; the rate of oxidation is 2.76 m. equ. per l. per min. The current efficiency must have fallen off from approximately 100% initially to 56%. A possible second steady-state was attained after 15 min. with 2.0 amps., for which the total rate of decomposition was calculated to be 2.36, the rate of oxidation 5.52, and the current efficiency, 43%.

Other Applications. Under any circumstances where it is desired to interpret the kinetics of reactions involving argentic silver in appreciable concentrations or to interpret steady-states, it is desirable to know the rate of reaction, as in the case of the ozone-silver work. It would be interesting to study more closely the direct oxidation of silver ion by persulfate, in the absence of any reducing agent other than water, for instance. In this connection, let it be mentioned that calculations of constants of the rate of decomposition

of argentic ion in 3 M H_2SO_4, 0.033 f. Σ Ag, based on observations of Hoard at 24°, give a value of k_2 of 0.18, almost exactly that for HNO_3 of the same molality, but k_4 turned out to be 18,000, about three times as great. Enhanced fourth-order reaction might account for the greater rate of decomposition as sulfuric acid becomes more concentrated.

Perhaps the most stable reagent of argentic silver that could be prepared at room temperature would be a solution of 9.4 N HNO_3 saturated with $AgNO_3$, as in stronger acid the concentration of monovalent silver falls off rapidly from the value of 0.6 prevailing there. Argentic ion in concentration of 0.01 N would decompose at a rate of only 2% per hour. A solution of 0.005 N decomposes only one fourth as rapidly, and one of 0.001 N decomposes only at about 0.5% per day.

Nature of Reactions Involving Solids

Free Energies. It seems worthwhile to correlate what is known about the stabilities of various compounds of oxidized silver. The calculations made in these two subdivisions do not rest on any measurements I have carried out, but a large number have never been made before, and the collection of these in one place may facilitate experiment.

The electrode potentials involving the two argentic oxides and argentous compounds, first studied by Luther and Pokorny (Ref. 3) have been confirmed by others. The most accurate measurements existing were made at 0°, and are represented here:

Pt, H_2 / KOH (1 m.) / AgO, Ag_2O, Pt. $E = 1.437$ v. (a)

(Jirsa. Ref. 8b).

Pt, H_2 / KOH (1 m.) / Ag_2O_3, (AgO) ?, (Ag_2O ?), Pt. $E = 1.546$ v. (b)

Pt, H_2 / H_2SO_4 (0.5 m.) (0.05 m.) (0.005 m.) / H_2SO_4 (0.5 m.) (0.05 m.) (0.005 m.) /

Ag_2SO_4, Ag_2O_3, Ag, Pt. $E = \begin{matrix}(1.771\text{ v.}\\(1.741\text{ v.}\\(1.706\text{ v.}\end{matrix}$ (c)

(both from Carman, Ref. 6).

In addition, Noyes and Kossiakoff (Ref. 2c) determined the following:

Pt, H_2 / $HClO_4$ (H^+ = 1.00 m.) // HNO_3 (c m.),

$Ag^+ = Ag^{++}$, Pt. $E = 1.914$ v. (d)

To interpret these observations, there must be known the free energy of formation of H_2O and Ag_2O at 0°. The first of these may be calculated from the equation given by Lewis and

Randall (Ref. 9) as:

$$\Delta F^{\circ}_{273}\ (H_2O) = \underline{-57,540\ \text{cal.}}$$

For Ag_2O, ΔF°_{298} = -2,395 cal. and ΔH = -6,950 cal. were taken from the International Critical Tables. Using the second-law free energy equation:

$$\Delta F^{\circ}_{273}\ (Ag_2O) = \underline{-2,780\ \text{cal.}}$$

Cell (a) evidently involves the reaction:

$$H_2 + 2\ AgO \longrightarrow Ag_2O + H_2O.\quad -\Delta F = 2 \times F \times 1.437$$
$$= 66,270\ \text{cal.} \qquad (e)$$

from which it is seen that:

$$\Delta F^{\circ}_{273}\ (AgO) = \underline{+2,980\ \text{cal.}}$$

It is not so obvious which reaction is involved in cell (b):

$$H_2 + Ag_2O_3 \longrightarrow 2\ AgO + H_2O.\quad -\Delta F = 2 \times F \times 1.546$$
$$= 71,290\ \text{cal.} \qquad (f_1)$$

or,

$$2\ H_2 + Ag_2O_3 \longrightarrow Ag_2O + 2\ H_2O.\quad -\Delta F = 4 \times F \times 1.546$$
$$= 142,580\ cal. \qquad (f_2)$$

The first of these gives a value of +19,680 for $\Delta F^{\circ}_{273}\ (Ag_2O_3)$, and the second a value of +24,720. Using the value deduced from the first equation (f_1) and the other known free energies involved, the free energy change for reaction (f_2) is calculated to be -137,540, corresponding to a decomposition voltage for the reaction of 1.49 volts, which is not observed, the voltage of cell (b) falling, after a short time in which Ag_2O_3 decomposes, without break to that of cell (a).

Thus we take:

$$\Delta F^{\circ}_{273}\ (Ag_2O_3) = +24{,}720 \text{ cal., provisionally.}$$

The interpretation of cell (c) is also not self-evident. A ten-fold change in the formality of the sulfuric acid works respectively 0.030 and 0.035 volts decrease in E.M.F. Reaction (f_1) above cannot be the cause of the reaction because its E.M.F. is independent of acidity. Assuming as a first approximation that the second hydrogen of sulfuric acid is only negligibly ionized, the other two reactions are possible:

$$H_2 + 2\ AgO + H^+ + HSO_4^- \longrightarrow Ag_2SO_{4(s)} + 2\ H_2O. \qquad (g_1)$$

and

$$2\ H_2 + Ag_2O_3 + H^+ + HSO_4^- \longrightarrow Ag_2SO_{4(s)} + 3\ H_2O. \qquad (g_2)$$

For (g_1) $E = E_o - \frac{.0542}{2}\log\frac{1}{c2}$, or the observed potential should decrease .054 volts for a ten-fold decrease in sulfuric acid concentration. Were the acid completely ionized, the change would be three-halves as great, or .081 volts, which does not correspond to fact.

For (g_2), $E = E_o - \frac{.0542}{4}\log\frac{1}{c2}$, or a change of .0271 volts for a ten-fold change of acid. For completely ionized acid this should be .0407, a value which the observed one seems to be approaching. Thus, the cell reaction involves the reduction of Ag_2O_3 to Ag_2SO_4, a fact which Carman deduced by a roundabout calculation. For the three concentrations of H_2SO_4, the free energy changes are:

$$2\ H_2 + Ag_2O_3 + H_2SO_4 \begin{matrix}(0.5\ \text{m.})\\(0.05\ \text{m.})\\(0.005\ \text{m.})\end{matrix} \longrightarrow Ag_2SO_4 + 3\ H_2O. \quad -\Delta F = \begin{matrix}(163{,}320)\\(160{,}560)\\(157{,}340)\end{matrix} \text{ cal.}$$

(h)

Carman measured also the cells at 0°:

$$\text{Pt, } H_2 \text{ / } H_2SO_4 \begin{matrix}(0.5 \text{ m.})\\(0.05 \text{ m.})\\(0.005 \text{ m.})\end{matrix} \text{ / } H_2SO_4 \begin{matrix}(0.5 \text{ m.})\\(0.05 \text{ m.})\\(0.005 \text{ m.})\end{matrix} \text{ / } Ag_2SO_{4(s)}, \text{ Ag.} \qquad (j)$$

for which he observed respectively 0.747, 0.802 and 0.851 volts. Cell reactions with free energy changes are :

$$H_2 + Ag_2SO_4 \longrightarrow 2\ Ag + H_2SO_4 \begin{matrix}(0.5 \text{ m.})\\(0.05 \text{ m.})\\(0.005 \text{ m.})\end{matrix} \qquad -\Delta F = \begin{matrix}(34,440)\\(36,980)\\(39,240)\end{matrix} \text{ cal.} \qquad (k)$$

Adding reaction (k) to reaction (h) and the corresponding free energies, we have:

$$3\ H_2 + Ag_2O_3 \longrightarrow 2\ Ag + 3\ H_2O. \qquad -\Delta F = \begin{matrix}(197,760)\\(197,540)\\(196,580)\end{matrix} \text{ cal.} \qquad (m)$$

These values are in fair agreement. From reaction (m) we calculate three values for the free energy of Ag_2O_3, namely +25,140, +24,920 and +23,960 cal., respectively. Dropping the last value because of the great dilution of acid and probable greater difficulty in measurement, we take the mean including the value from reaction (f_2) of +24,720 to obtain:

$$\Delta F^\circ_{273} \quad (Ag_2O_3) = \underline{+24,930 \text{ cal.}}$$

For the last $-\Delta F$ of set (m), the formality of Ag_2SO_4 is about five times that of H_2SO_4 and liquid junctions may not have been made reprodicibly so that they would cancel when treating cells (c) and (j) together.

Bray and Hershey (Ref 11.) give a newly calculated value of the molal electrode potential of Ag^+ against Ag of -0.7985, from which ΔF°_{298} (Ag^+) = +18,410 cal. is calculated. Using

ΔH = +24,490 cal. from the International Critical Tables, it is calculated:

$$\Delta F^{\circ}_{273}\ (Ag^{+}) = \underline{+18,920\ cal.}$$

Using this value in connection with the free energy decrease connected with cell (d), +44,130 cal., and including the activity coefficients involved in 1 m. HNO_3, we obtain:

$$\Delta F^{\circ}_{273}\ (Ag^{++}) = \underline{+63,050 + 1,249 \log_{10} \frac{a+}{a++}\ cal.}$$

The exact value of this activity correction will be difficult to determine, but it will be a positive correction.

A very crude estimate of the activity coefficient of a divalent ion (Ba^{++}) in ionic strength 1 has been made by Coryell and Yost. (Ref.12), yielding the value of 0.11, which may be low for the Ag^{++} ion. The Ag^{+} ion will probably have a coefficient of the order of 0.6, or about five times as great. Thus, it is seen that the activity correction may amount to about 870 calories. The fact that the E. M. F. of cell (d) did not change sensibly with the change of concentration of HNO_3 indicates that both ions have nearly their minimum activity coefficients over the range and are effectively constant or that they are changing together. A fair value for $\Delta F^{\circ}_{273}\ (Ag^{++})$ is $\underline{+63,900\ cal.}$, with somewhat larger probable error than the other values have.

Jirsa (l. c.) observed that the E.M.F. of cell (a) at 30.2° also, obtaining 1.428_6 volt. This gives $\frac{d\ E}{d\ T} = 0.00028$. Taking an interpolated value of the E.M.F. at 25° = 1.430 v., and a value for the heat content of $H_2O_{(\ell)}$ = -68,420, it is seen:

$$AgO: \quad \Delta F^{\circ}_{298} = \underline{+3,490\ cal.}\ ; \quad \Delta H_{298} = \underline{-2,760\ cal.}$$

In spite of his risky extrapolations, the heat of the formation of AgO found calorimetrically by Jirsa, 2,980 cal., is almost identical with the value given above, which is, however, far more accurate, and which he could have calculated from his potentiometric observations.

Unfortunately the change in heat content associated with the other reactions here discussed cannot be accurately determined because of lack of experimental data.

Predicted Interrelationships and Equilibria. On the basis of the free energies at 0° degrees derived above, the E:M.F. of the following cell may be calculated as 1.654 volts:

Pt, H_2 / KOH / Ag_2O_3, AgO, Pt.

If one should oxidize a small amount of silver on a platinum wire at an anode, the following decomposition potentials should be observed:

1.187 v. $Ag \longrightarrow Ag_2O$
1.437 v. $Ag_2O \longrightarrow AgO$
1.546 v. $Ag_2O \longrightarrow Ag_2O_3$
1.654 v. $AgO \longrightarrow Ag_2O_3$

If, then, at each potential one oxidizes the substance as far as it will go, beginning with the first, when the third potential is reached, there will be no Ag_2O left, so no change can occur, and the voltage must be raised to 1.654 V. However, since no Ag_2O_3 is formed in basic solution, it is obvious that the oxygen overvoltage has been exceeded. It should be possible, perhaps with the purest Ag_2O_3 obtainable, to observe the last potential listed.

The dismutation of AgO to solid products:

$$4\ AgO \longrightarrow Ag_2O_3 + Ag_2O \qquad (n)$$

involves a free energy decrease of -10,230 cal., and therefore does not take place. The dismutation in acid solution:

$$4\ AgO + 2\ H^+ \longrightarrow Ag_2O_3 + 2\ Ag^+ + H_2O \qquad (o)$$

involves a free energy decrease of+6,690 cal., and has an equilibrium constant:

$$\frac{(Ag^+)}{(H^+)} = K_D = 4.8 \times 10^2$$

This serves to emphasize the inherent instability of AgO. That it is formed in acid solutions indicates that Ag_2O_3 decomposes at an appreciable rate; indeed the decomposition pressure of oxygen over a mixture of Ag_2O_3 and AgO is calculated to be 4.0×10^{30} atm. AgO itself has a decomposition pressure of 6.0×10^{11} atm. decomposing to Ag_2O, but seems to be relatively non-reactive. Its acid properties are not very great, for the equilibrium constant for the reaction:

$$AgO + H^+ \dashrightarrow H_2O + Ag^{++} \qquad (p)$$

is 2.0×10^{-3}.

One of the most interesting reactions is the dismutation of the divalent ion into tervalent oxide and monovalent ion:

$$4\ Ag^{++} + 3\ H_2O \dashrightarrow Ag_2O_3 + 2\ Ag^+ + 6\ H^+$$

for which the free energy decrease is +20,210 cal.; the probable error is much greater here due to the participation of four argentic ions. The equilibrium constant is calculated to be:

$$\frac{(Ag^+)\ (H^+)^3}{(Ag^{++})^2} = K_{Dis} = 1.2 \times 10^8$$

For an appreciable concentration of argentous ion in dilute acid this equilibrium limits the concentration of argentic ion to lower values than any other equilibrium considered. It is very probable that experiments being conducted at my suggestion by Mr. DeVault will measure this equilibrium, if any equilibrium is involved in the complexity of steady states. The effect of activity coefficients to raise the argentic concentration must be remembered.

A reaction of considerable importance is the oxidation of water to ozone by argentic ion. Using the value $\Delta F^{\circ}_{298}\ (O_3)$ = +38,900 cal. taken from Kassel (Ref. 13) and the value $\Delta H_{298}\ (O_3)$ = 33,920 (Ref. 14):

$$\Delta F^{\circ}_{273}\ (O_3) = \underline{+38{,}400 \text{ cal.}}$$

Therefore for the following reaction:

$$2\ Ag^{++} + H_2O + O_2 \dashrightarrow 2\ Ag^{+} + 2\ H^{+} + O_3 \qquad (q)$$

the free energy decrease is -6,000 cal., but not up to the point where the reaction might be expected to go appreciably. In fact, for the reaction as written, the equilibrium constant is 1.6×10^{-5}; when argentous activity is ten times argentic and hydrogen ion is 1 molal, the partial pressure of ozone is 1.6×10^{-7} atm. in equilibrium with the solution.

Somewhat surprising is the relationship for the following:

$$6\ Ag^{++} + 3\ H_2O \text{ ---} 6\ Ag^{+} + 6\ H^{+} + O_3 \qquad (r)$$

where the free energy decrease is +58,860 cal., indicating that the reaction has a great tendency to go. No chemical evidence exists however that any of six or eight oxidizing

agents capable of oxizing water to ozone by the analagous equation do so.

A piece of pure speculation is the prediction of properties of the tervalent ion, indicated from kinetic evidence to be perhaps AgO^+. However, from the consistence of the measurements of cell (d) an upper limit of its concentration may be set at 20% of the total argentic equivilents. Assuming $H^+ = 1.0$, $Ag^+ = 0.04$, $Ag^{++} = 0.003$, and $AgO^+ = .0008$ Nor 0004 m. in the following equilibrium:

$$2\ Ag^{++} + H_2O \dashrightarrow AgO^+ + Ag^+ + 2\ H^+ \qquad (s)$$

a maximum equilibrium constant of approximately 1 is obtained. This maximum K_3 must not be inconsistent with the observations of the state of oxidation in strong nitric acid (Ref. 2b) mentioned on P. 9 of this paper. Taking a lower limit for H^+ as 15, taking Ag^+ as 0.04 and Ag^{++} as 0.3 the maximum value for AgO^+ turns out to be 0.01, somewhat more than would be expected to go unobserved. Since the hydrogen ion activity is undoubtedly much greater, the value for maximum K_3 is probably admissable.

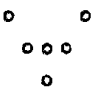
Equation (s) yields a minimum free energy for AgO^+ of +51,000 cal. The calculated electrode potential, $Ag^+ + H_2O \rightarrow$ $\dashrightarrow AgO^+ + 2\ H^+$ turns out to be -1.94 volts as a maximum value (Minimum negative value).

Reaction (t):

$$Ag_2O_3 + 2\ H^+ \dashrightarrow 2\ AgO^+ + H_3O \qquad (t)$$

is accompanied by a free energy decrease of -19,000 cal. The

ratio $\frac{(AgO^+)}{(H^+)}$ in this equilibrium is about 10^{-7} as a maximum. Too much value must not be placed on these qualitative considerations of the hypothetical ion AgO^+.



I wish to express my sincere appreciation to Dr. Noyes for this opportunity to have worked with him on the silver research and for his continued interest in me and in my work. Other members of the department, especially Dr. Swift, have been most helpful in many discussions concerning this research.

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